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A Quality Assurance Program for Monitoring Ozone and Carbon Monoxide

Radian Corp, Austin, Tex

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A QUALITY ASSURANCE PROGRAM FOR MONITORING OZONE AND CARBON MONOXIDE

JUNE 1977
FINAL REPORT

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION VI
SURVEILLANCE AND ANALYSIS DIVISION
DALLAS, TEXAS 75270

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16. ABSTRACT

This report describes a quality assurance program for monitoring ozone and carbon monoxide using a chemiluminescent ozone monitor and a non-dispersive infrared CO monitor. Instrument selection criteria and site selection criteria are presented. Step-by-step procedures are given discussing routine station operation, instrument multi-point calibrations, and quality assurance audits. Record keeping procedures and data reduction and data handling are discussed.

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A QUALITY ASSURANCE PROGRAM FOR MONITORING OZONE AND CARBON MONOXIDE

FINAL REPORT

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1.0 INTRODUCTION

Many factors are important in the collection of acceptable air quality data. These factors include stable, well-maintained instruments, a suitable environment for those instruments, a well-designed sampling system that provides unaltered samples of the ambient air, reliable reference gases, detailed records of all activities, proper operating procedures and proper siting of the monitors. In addition, it is essential to perform periodic calibrations and control sample audits to assess the uncertainty in the ambient data.

The importance of data quality cannot be overemphasized. Data which cannot be substantiated are of little use. It is increasingly necessary that air monitoring data withstand challenge in courts of law. All personnel, from station technicians to supervisory and management personnel, need to follow those quality assurance procedures required to generate high quality ambient air data.

The purpose of this manual is to describe a quality assurance program that will produce acceptable, defendable ambient measurements of carbon monoxide (CO) and/or ozone (O_3). It is directed to any agency using chemiluminescent ozone monitors and/or non-dispersive infrared (NDIR) CO monitors.

2.0 QUALITY ASSURANCE PROGRAM FOR MONITORING OZONE

2.1 Selection of Ozone Monitoring Equipment

The current Federal Reference Method for the measurement of ozone is the chemiluminescent method involving the reaction of ozone and ethylene. This type monitor should be preferred. Selection of a particular instrument should be based on that instrument's specifications and cost. In general, instrument specifications should meet or exceed the following EPA requirements (References 1 and 2):

A. Operating Range (0-0.5 ppm)

B. Noise (0.005 ppm)

C. Lower Detectable Limit (0.01 ppm)

D. Interference Equivalent
   Each Interference - ±0.02 ppm
   Total Interference - 0.06 ppm

E. Zero Drift (12 and 24 Hour) - ±0.02 ppm

F. Span Drift (24 Hours)
   20 Percent of Upper Range Limit - ±20.0%
   80 Percent of Upper Range Limit - ±5.0 %

G. Lag Time (20 Minutes)

H. Rise Time (15 Minutes)

I. Fall Time (15 Minutes)

J. Precision
   20 Percent of Upper Range Limit - 0.01 ppm
   80 Percent of Upper Range Limit - 0.01 ppm

3.2 Site Selection and Installation of Equipment

Site selection criteria for ozone monitoring are discussed in the EPA Guideline Series OAQPS No. 1-2-012 (Reference 3). One primary concern in site selection for ozone is to avoid the scavenging effect of NO emissions, vegetation, and building surfaces. Peak ozone levels occur about 15 to 25 kilometers downwind of major urban areas. Thus, peak level sites should be located in areas downwind of the central business district (CBD) of urban areas. An upwind site is also recommended to monitor incoming ozone. Major traffic arteries or large parking areas should be at least 100 and preferably 200 meters away. Separations of 20 to 50 meters from vegetation sinks and at least one meter from building surfaces are desirable for final probe placement. Either ground level or rooftop sampling is acceptable because ozone is well mixed vertically.

The ozone analyzer should be housed in an environment that provides protection from the weather, a controlled, stable temperature environment, a voltage regulated power supply, and a suitable sample introduction system. Manufacturer's specifications will indicate the allowable temperature and voltage ranges that must be maintained for acceptable analyzer performance. The acceptable temperature range for EPA-approved instruments is 20-30°C (68-86°F); the acceptable voltage range is 105 to 125 volts (Reference 2). A continuous record of shelter temperature and voltage should be made, and if variations beyond the acceptable limits occur during any period, all data collected during that period must be voided.

The sample introduction system should consist of an intake port (isolated from any interferences such as vent ports, or O_3 sinks), a moisture and particulate trap, and a sample manifold and exhaust blower. The materials in contact with the

ambient sample should be inert to ozone; glass and teflon are acceptable. Care should be taken that moisture does not condense in the sampling system as this will invalidate ozone measurements. If a particulate filter is used in the sampling system, it must be replaced frequently to avoid sample contamination. Weekly replacement is recommended.

The sample manifold volume should be sufficient to prevent pressurisation or creation of a vacuum in the manifold when a sample is being drawn by the analyser. A manifold air flow rate of three to five times the total sample requirements of all monitors connected to the system is desirable. The excess manifold flow is vented to ambient (Reference 4).

The installation of an ozone analyser will depend on the specific station configuration. (An example of a properly designed ozone system is shown in Figure 1.) The instrument manufacturer's installation procedures should be followed where possible. Some modifications may be necessary to accommodate a particular station configuration. In general, however, the following should be adhered to:

- Become familiar with and practice all precautionary measures for handling ethylene.
- ETHYLENE IS HIGHLY EXPLOSIVE
- The ethylene cylinder should be firmly secured to prevent any movement that might introduce leaks in the line.
- Use stainless steel tubing to connect the ethylene cylinder to the ozone analyser. Check all connections for leaks.

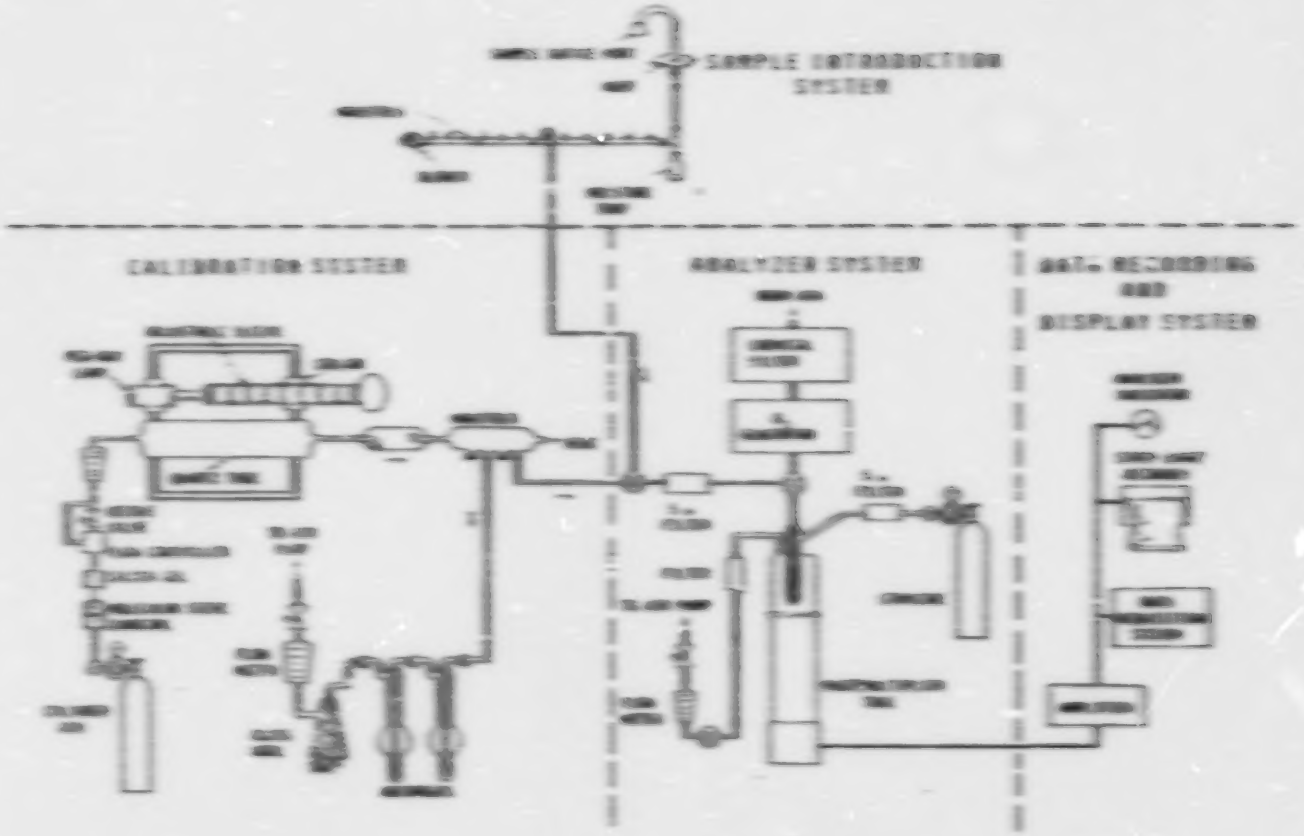

FIGURE 1. OZONE MONITORING SYSTEM FLOW CHART
(Reference 5)

- Use only teflon tubing and teflon fittings to connect the ambient sample manifold port to the analyser.

- Connect the analyser exhaust vent to a suitable vent to ambient. The vent should be widely separated from the ambient manifold intake.

- Make the proper electrical connections to the data storage system used with the ozone analyser. Specific instructions are provided by the instrument manufacturer for connecting the analyser output signal to a strip chart recorder or a remote system, such as a computer, microprocessor or data logger. If a recorder is used, it should be properly calibrated (see Section 2.4.2).

- If the ozone analyser does not contain an internal ozone generator, an external O_3 source will be necessary. Follow the instrument manufacturer's directions for installing the generator.

Instrument start-up and checkout should be performed after proper installation is completed. The following steps should be performed in sequence:

(1) Connect the analyser power cord to a regulated 115 volts AC, 60 Hz power supply.

(2) Adjust the ethylene cylinder regulator to obtain the second stage pressure recommended by the manufacturer (usually 30 to 40 psig).

(3) Adjust the analyser TIME CONSTANT SELECTOR switch to the manufacturer's recommended setting for start-up operations (usually a mid-range setting).

(4) Adjust the RANGE SELECTOR switch to the 0.5 ppm position.

(5) Place the MODE SELECTOR switch in the ZERO mode.

(6) Turn the POWER switch ON. Verify the analyser is operating by observing the POWER indicator switch illumination, the cooling fan operation, and the SAMPLE PLUS ETHYLENE flow meter reading.*

(7) After a warm up period of at least two hours, adjust the SAMPLE PLUS ETHYLENE needle valve (or the air and ethylene valves if so equipped) to obtain the flow rate(s) specified on the manufacturer's data sheet (supplied with the analyser).

---

*Some analysers have separate air and ethylene rotameters. For these instruments, each rotameter should be adjusted according to the manufacturer's specifications.

(8) Verify the ethylene flow rate by connecting an appropriate flow measuring device (bubble meter, calibrated rotameter, or mass flow meter) to the PULL TO TEST diverter valve. If the ethylene flow does not agree with the data sheet specification (Step G) with the regulator adjusted to the specified pressure (Step H), check all connections for leaks. Also, check the ethylene line sintered filter for possible blockage. If no plumbing problems are found, adjust the pressure regulator to obtain the manufacturer's recommended ethylene flow rate.

(9) Place the TIME CONSTANT SELECTOR switch in the highest setting (40 seconds).

(10) Place the RANGE SELECTOR switch in the most sensitive position (normally 0.01).

(11) Unlock the ZERO adjustment control and adjust it for an exact zero reading on the O_3 concentration meter. Lock the ZERO control.

(12) Place the RANGE SELECTOR switch in the 0.5 position.

(13) Set the MODE SELECTOR switch to the CALIBRATE (or SPAN) position. Allow at least 15 minutes for the analyzer to stabilize.

(14) Unlock the CALIBRATE (SPAN) control and adjust it to obtain the O$_3$ CONCENTRATION indication specified by the manufacturer on the supplied data sheet (or to the concentration of the external generator if so equipped). Lock the CALIBRATE (SPAN) control.

(15) Set the MODE SELECTOR switch to ZERO.

(16) Turn the POWER switch OFF.

If the analyzer will be inoperative for any length of time, shut off the ethylene cylinder valve.

After the initial checkout has been completed and prior to ambient sampling, a primary calibration of the analyzer should be performed according to procedures detailed in Section 2.4.

2.3 Routine Operation Procedures

The collection of ambient air ozone data can begin following the installation, checkout, and proper calibration of the ozone analyzer and data recording system. The analyzer may operate unattended for periods as long as a week or as short as 24 hours (or less), depending upon the particular monitoring program. Regularly scheduled visits must be made by the station operator to check the system and perform necessary maintenance.

The following discussion describes those routine operation procedures which will help produce high levels of quality assurance. It is assumed that the ozone monitor has been properly calibrated and previously placed in operation.

(1) Upon arrival at the station (monitoring site), make an entry in the instrument (or station) log book. Include the date, time, purpose of visit, and operator's initials.

(2) Record the unadjusted zero and unadjusted span control settings in the log. Compare the unadjusted zero with the adjusted zero setting recorded during the previous station visit. If there is a difference, note it in the log and notify your supervisor. Make a notation on the strip chart record to mark the end of the ambient data record for the previous sampling period.

(3) Record the first and second stage pressures from the ethylene cylinder regulator in the log.

(4) Read and record the UNADJUSTED AIR PLUS ETHYLENE FLOW. (If the analyser has separate air and ethylene rotameters, read each and record as UNADJUSTED AIR and UNADJUSTED ETHYLENE, respectively.)

(5) Turn the MODE SELECTOR switch to SPAN (CALIBRATE). Wait approximately 15 minutes until the analyser response has stabilised. Label the strip chart record "Unadjusted Span". (Include the date and time on the chart for reference.)

(6) Record the stabilized, unadjusted span output for about five minutes. Convert the chart reading into a ppm value and record in the log book as the UNADJUSTED SPAN.

(7) Put the MODE SELECTOR switch to ZERO. Wait approximately 15 minutes for the analyzer response to stabilize. Label the strip chart record "Unadjusted Zero".

(8) After the response has stabilized, take a five minute zero reading. Convert the chart reading to ppm and record in the log as UNADJUSTED ZERO.

(9) Calculate the percent drift in the span response as follows:

$$\text{Span Drift (\%)} = 100 \times \frac{\text{unadjusted span (ppm)} - \text{previous adjusted span (ppm)}}{\text{previous adjusted span (ppm)}}$$

(The previous adjusted span (ppm) was obtained during the last station visit and recorded in the log book.)

Likewise, calculate the Zero Drift from the unadjusted zero (ppm) and previous adjusted zero.

Compare the span and zero drift (%) to accepted drift limits.* If either the

*Each agency should establish acceptable span and zero drift limits. Span or zero drift in excess of these limits would require invalidating all ambient data collected during this period from the last acceptable ZERO/SPAN to the present.

span or zero drift exceeds the allowable limit, make note of this on the strip chart record and notify the supervisor.

(10) Perform a complete system check. Inspect all lines for leaks or loose connections. Check for dirt or moisture in the sample manifold or ambient sample line. If the sample manifold has a blower, check to insure it is operating. If the station is equipped with a temperature and/or voltage recorder, check for evidence of excessive fluctuations that would invalidate the ambient data collected since the last visit. Check the strip chart record for evidence of instrument problems. Record all observations in the station log. MAKE NOTE OF ALL ADJUSTMENTS AND/OR REPAIRS.

(11) Perform all necessary and scheduled maintenance. This would include checking and/or replacing the ambient sample filter, the ethylene sintered filter, the zero air chemical filter, ethylene cylinder replacement, etc. Specific instrument manufacturer's instructions for instrument maintenance requirements should be incorporated into the routine procedures at the manufacturer's recommended intervals.

(12) Check the recorder for proper chart speed and gain control setting. Replace

the strip chart paper, if necessary. Check the ink supply and replenish, if necessary. Clean the pen, if needed.

(13) Check the AIR PLUS ETHYLENE rotameter reading. If the flow is different from the manufacturer's recommended setting, adjust to the correct value. Record the flow in the log, as ADJUSTED AIR PLUS ETHYLENE flow. (If the instrument has separate air and ethylene rotameters, adjust each, if necessary, to the correct flow and record appropriately in the log.)

(14) Turn the MODE SELECTOR to ZERO. Allow the instrument to stabilize. Adjust the ZERO adjustment control to obtain a zero output. Adjust the recorder zero adjustment to obtain a zero trace at five percent full scale. (If the recorder chart has an offset baseline, adjust to this point.)

(15) Record a five minute segment at the final zero adjustment. Record the adjusted zero value in the log and label the recorder trace ADJUSTED ZERO.

(16) Turn the MODE SELECTOR switch to SPAN (CALIBRATE). Wait until the instrument response has stabilized.

(17) Record a five minute segment at the final span level. Record the new span value in

the log as the adjusted span. Label the recorder segment "ADJUSTED SPAN".

(18) Turn the MODE SELECTION switch to SAMPLE. Wait until the instrument response has stabilized (about 15 minutes). Mark the chart record at this point "BEGIN AMBIENT/(DATE)/(TIME)/(INITIALS)". Record the recorder chart speed and gain control setting on the strip chart and in the log.

2.4 Routine Calibration Procedure

Primary calibration of an ozone analyzer should be performed:

(1) When the instrument is first installed at a site.

(2) At regular intervals (monthly is recommended) as long as the analyzer is in operation.

(3) When maintenance has been performed that could affect the response characteristics.

(4) When audit results indicate unsatisfactory performance.

The calibration of an ozone analyzer is performed by adjusting the analyzer/recorder response to a known source of ozone at several concentration levels. An external ozone generator is required. Other equipment required includes:

(1) Cylinder of air for the generator.

(2) Spectrophotometer and calibration curve.

(3) KI bubbling train (the all glass impingers should be midget impingers. Specifications for the midget impinger are given in Figure 2).

(4) Flow meter or calibrated rotameter.

(5) Miscellaneous glassware (flasks, burette, pipets, etc.).

(6) Chemical reagents required for an NBKI standardization (see Appendix J, EPA Reference Method).

(7) Stopwatch or electric timer.

Due to shortcomings with the one percent NBKI procedure, the EPA is considering amending the photochemical oxidant calibration procedure (Federal Register, Volume 41, No. 195, Wednesday, October 6, 1976). Alternative methods that are being evaluated are: (1) a revised version of the KI procedure; (2) gas phase titration (GPT) with NO, and (3) ultraviolet absorption (UV). Air monitoring agencies should follow EPA's interpretation of the NBKI calibration procedure until the final promulgation of appropriate amendments to Appendix D of 40 CFR Part 50. This procedure is explained in detail below. Additionally, all recorders and flow meters should be periodically calibrated. Detailed procedures are outlined below.

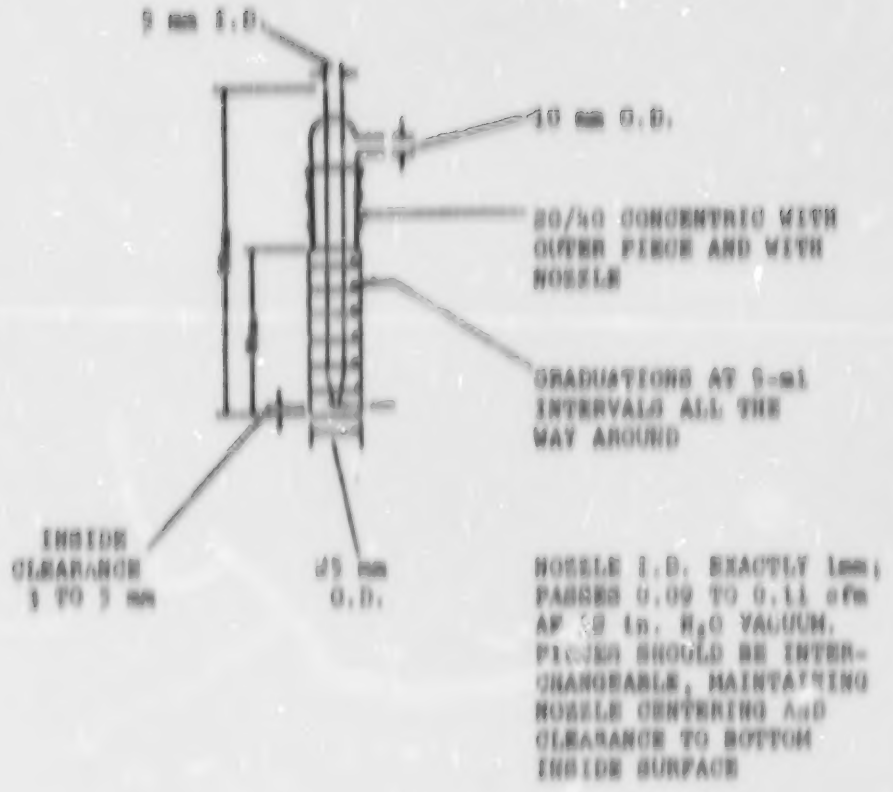
9 mm I.D.
10 mm O.D.
20/40 CONCENTRIC WITH OUTER PIECE AND WITH NOZZLE
GRADUATIONS AT 5-ml INTERVALS ALL THE WAY AROUND
INSIDE CLEARANCE 4 TO 5 mm
45 mm O.D.
NOZZLE I.D. EXACTLY 1mm; PASSES 0.09 TO 0.11 cfm AT 10 in. H2O VACUUM. PIECES SHOULD BE INTERCHANGEABLE, MAINTAINING NOZZLE CENTERING AND CLEARANCE TO BOTTOM INSIDE SURFACE

FIGURE 2

MIDGET IMPINGER SPECIFICATIONS

2.4.1 Routine Analyser Calibration

NOTE: If the analyser has been routinely collecting ambient data, perform a ZERO/SPAN operation (Steps 1-13 of Section 2.3) before proceeding to Step 1 below:

(1) Set up an external ozone generator and connect to a clean air system. Figure 1 illustrates an appropriate set up.

(2) Plug in the spectrophotometer and turn the POWER switch ON.

(3) Turn the ozone generator power switch ON and allow the generator to stabilise (readings ten minutes apart should not differ by more than 1.0% to 2.0%).

(4) Connect the generator output to a sampling manifold. Connect one port of the manifold to the station vent. Cap all other manifold ports. Use teflon tubing for all sample lines. (The vent line does not need to be teflon but should be of sufficient diameter to prevent restriction of the excess vent flow.)

(5) Connect a bubble meter, mass flow meter or calibrated rotameter in-line between the ozone generator and the manifold.

(6) Adjust the generator output to obtain a flow rate that is at least 50% greater than the sum of the ozone analyser's sample flow rate and the KI bubbling train flow requirements. (For example, if the analyser sample flow was one liter/minute and the bubbling train flow was one liter/minute, the generator output flow rate should be set to >3 liters/minute.)

NOTE: If the calibration is being performed on an instrument that has been monitoring ambient air quality, an unadjusted ZERO/SPAN should be performed at this point.

(7) Verify that the ozone analyser POWER switch is ON. Place the MODE SELECTOR switch to ZERO. Wait until the response has stabilized. Unlock the analyser ZERO ADJUSTMENT control and adjust the analyser to obtain a zero reading on the O_3 CONCENTRATION meter on the analyser. Adjust the recorder ZERO ADJUST control to obtain a reading at 5% full scale on the strip chart. (If the chart has an offset zero, adjust to this baseline.)

(8) Set the analyser RANGE switch to 0.5 ppm. Place the MODE SELECTOR switch to SAMPLE.

(9) Disconnect the analyser ambient sample line from the station ambient manifold.

Cap the ambient port. Inspect the sample line tubing to insure that it's clean and dry. If the tubing is dirty or is suspected of scrubbing out ozone, then it should be replaced with new teflon tubing. Connect the sample line to a spare port on the ozone generator manifold.

(10) Identify the strip chart record as ANALYZER CALIBRATION.

(11) Adjust the generator sleeve setting to obtain an analyzer response of about 80% full scale (~0.4 ppm).

(12) Connect the KI bubbler train inlet to a spare port on the ozone generator manifold.

(13) Connect the two bubbler tubes of the KI bubbling train in series. Connect this series to the demister, the demister to the bottom of a calibrated rotameter, the top of the rotameter to a flow controller and the flow controller to the KI bubbling train vacuum pump.

(14) Turn on the pump and adjust the flow controller to give a rotameter reading of 1000 cc/minute. Make sure a positive flow is maintained at the ozone generator manifold vent. Turn off the pump.

(15) Pipet 10 ml of the KI absorber into each of the two clean bubbler tubes and

reconnect the tubes in series in the bubbling train as in Step 13. The impingers should be dry, clean, and lint free.

(16) Turn on the bubbling train pump and simultaneously begin timing a ten minute run. Adjust the flow controller to give a rotameter reading of exactly 1000 cc/minute.

(17) Record the ozone analyzer response (percent chart deflection) in the log book (calibration section) and on the calibration data sheet (Figure 3). Record the ozone generator sleeve setting similarly.

(18) Adjust the spectrophotometer to 352 nm. The spectrophotometer must be adjusted with a zero and a blank. The zero check is made with no sample in the sample port. The blank adjustment is made with a cuvette containing NBKI solution. Rinse the spectrophotometer cuvette with unbubbled KI absorber. Fill the cuvette with unbubbled absorber, place the cuvette in the spectrophotometer, and adjust the spectrophotometer to read 0.00 absorbance.

(19) After exactly ten minutes, turn the bubbler train sample pump OFF. Disconnect the bubbler tubes from the bubbling train.

SAMPLING STATION NAME/NUMBER_____ DATE_____

ANALYZER MODEL_____ SERIAL NUMBER_____

OZONE GENERATOR MODEL_____ SERIAL NUMBER_____

TYPE OF CALIBRATION: PRIMARY ☐ SECONDARY ☐

OPERATOR_____

ANALYZER ZERO CONTROL SETTING_____

ANALYZER SPAN CONTROL SETTING_____

Calibration Point	Generator Sleeve Setting (mm)	Ozone Concentration By KI (ppm)	Analyzer Response (% chart deflection)
1			
2			
3			
4			
5			
6			

FIGURE 3
OZONE CALIBRATION DATA SHEET
(Reference 5)

(20) Empty the cuvette. Rinse the cuvette with a small portion of the absorber from the second bubbler (trap). Then fill the cuvette to the mark with the bubbled absorber from the trap. Measure the absorbance on the spectrophotometer. Record this absorbance in the log book. The absorbance readings should be taken immediately after the end of the bubbling.

(21) Measure the absorbance of the remaining bubbler using the technique described in Step 20.

(22) Add the two absorbances (Steps 20 and 21) to obtain the total absorbance, A.

(23) Rinse the cuvette, bubbler tubes, glass impingers and 10 ml pipet with deionized or distilled water.

(24) Rinse the 10 ml pipet with unbubbled KI absorber. Then pipet 10 ml of fresh absorber into each bubbler tube.

(25) Reconnect the bubbler tubes to the sampling train and begin a second ten minute run.

(26) Compute the ozone concentration as follows:

$$O_3 \text{ (ppm)} = \left[\frac{A \times B \times (t+273)}{F \times T \times P}\right] \times 1.3$$

where:

F = bubbling train flow rate in cc/minute,

A = the absorbance from Step 22,

B = spectrophotometer factor for ozone (see Section 2.4.4),

P = the absolute (uncorrected for sea level) atmospheric pressure (in mm Hg),

T = bubbling time in minutes, and

t = station temperature in °C.

The bubbling time T is ten minutes for ozone concentrations greater than 0.1 ppm. For concentrations less than 0.1 ppm, T is 15 minutes.

(27) Complete the second bubbling run after <u>exactly</u> ten minutes. Measure the absorbances of the two bubbler solutions as previously described. Calculate the ozone concentration as in Step 26.

(28) Compute the average ozone concentration from the two bubbling runs. If the difference between Run 1 and 2 is greater than 7% of the average of Run 1 and 2, then a third run must be made. The ppm values for the three runs will be

averaged, unless one run is obviously in error (in that case the two good runs are averaged).

(29) Unlock the analyzer SPAN ADJUSTMENT control. Adjust the span control until the recorder deflection corresponds to the correct percentage of chart as computed by:

$$\text{Percent of Chart} = \frac{(\text{ppm } O_3)_m}{(\text{ppm } O_3)_f} \times 100 + 5 \text{ (Percent Zero Offset)},$$

where:

$(\text{ppm } O_3)_m$ = average ozone concentration computed in Step 28.

$(\text{ppm } O_3)_f$ = full scale reading of ozone analyzer (0.5 ppm).

(30) Record the average ozone concentration in the log book and on the data sheet (Figure 3). Also, record the strip chart percent deflection.

(31) Repeat Steps 8 through 29 for the ozone generator set to produce an analyzer response of 20, 40, and 60 percent full scale on the 0.5 ppm range.

(32) Construct an analyzer response best-fit curve by plotting recorder response versus ppm ozone as shown in Figure 4.

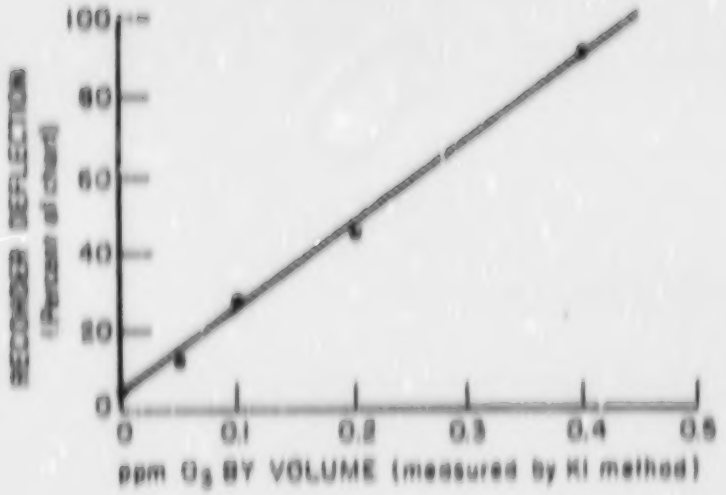

FIGURE 6
A SAMPLE OZONE ANALYZER CALIBRATION CURVE

(33) Calculate the percent deviation of each measured concentration as follows:

$$\text{Percent Deviation} = \frac{(\text{ppm } O_3)_m - (\text{ppm } O_3)_t}{(\text{ppm } O_3)_t} \times 100,$$

where:

$(\text{ppm } O_3)_m$ = measured ozone concentration.

$(\text{ppm } O_3)_t$ = ozone concentration from best fit curve for same recorder response as $(\text{ppm } O_3)_m$.

Identify any point deviating from the best fit curve by more than ±12 percent.

(34) Rerun any point deviating by more than ±12 percent from the best fit curve. Average the original and rerun values and replot. Reconstruct a best fit curve and check the deviation of all points. Continue in this manner until all measured points are within ±12 percent of the best fit curve.

(35) Fill out a calibration conversion table like that shown in Figure 5.

(36) Place the analyser MODE SELECTOR switch in the CALIBRATE (SPAN) position. Wait for the analyser response to stabilise.

(37) Read the analyser response from the recorder chart and label the recorder trace PROPER SPAN RESPONSE.

(38) Convert the PROPER SPAN RESPONSE from percent chart reading to ppm value using either the analyser calibration conversion table or the calibration curve.

(39) Record the PROPER SPAN RESPONSE (ppm) in the log book.

(40) Compute the span response drift (percent) from the current and previous PROPER SPAN RESPONSE (PSR) values:

$$\text{Proper Response Drift (\%)} = \frac{\text{PSR (current)} - \text{PSR (previous)}}{\text{PSR (previous)}} \times 100$$

Analyzer No. _____ Date of Calibration _____

% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM
0.0		10.5		40.5		60.5		80.5	
0.5		11.0		41.0		61.0		81.0	
1.0		11.5		41.5		61.5		81.5	
1.5		12.0		42.0		62.0		82.0	
2.0		12.5		42.5		62.5		82.5	
2.5		13.0		43.0		63.0		83.0	
3.0		13.5		43.5		63.5		83.5	
3.5		14.0		44.0		64.0		84.0	
4.0		14.5		44.5		64.5		84.5	
4.5		15.0		45.0		65.0		85.0	
5.0									
5.5		15.5		45.5		65.5		85.5	
6.0		16.0		46.0		66.0		86.0	
6.5		16.5		46.5		66.5		86.5	
7.0		17.0		47.0		67.0		87.0	
7.5		17.5		47.5		67.5		87.5	
8.0		18.0		48.0		68.0		88.0	
8.5		18.5		48.5		68.5		88.5	
9.0		19.0		49.0		69.0		89.0	
9.5		19.5		49.5		69.5		89.5	
10.0		20.0		50.0		70.0		90.0	
10.5		20.5		50.5		70.5		90.5	
11.0		21.0		51.0		71.0		91.0	
11.5		21.5		51.5		71.5		91.5	
12.0		22.0		52.0		72.0		92.0	
12.5		22.5		52.5		72.5		92.5	
13.0		23.0		53.0		73.0		93.0	
13.5		23.5		53.5		73.5		93.5	
14.0		24.0		54.0		74.0		94.0	
14.5		24.5		54.5		74.5		94.5	
15.0		25.0		55.0		75.0		95.0	
15.5		25.5		55.5		75.5		95.5	
16.0		26.0		56.0		76.0		96.0	
16.5		26.5		56.5		76.5		96.5	
17.0		27.0		57.0		77.0		97.0	
17.5		27.5		57.5		77.5		97.5	
18.0		28.0		58.0		78.0		98.0	
18.5		28.5		58.5		78.5		98.5	
19.0		29.0		59.0		79.0		99.0	
19.5		29.5		59.5		79.5		99.5	
20.0		30.0		60.0		80.0		100.0	

FIGURE 9
TABLE FOR CONVERTING TRACE DEFLECTION IN PERCENT OF CHART TO CONCENTRATION IN PPM
(Reference 5)

If the drift exceeds ±20% (or another limit established by your supervisor), notify the supervisor. Data obtained since the last calibration should be discarded.

(41) Disconnect the analyzer from the generator manifold and reconnect to the station ambient manifold.

(42) Put the MODE SELECTOR switch on SAMPLE. Wait until the analyzer response has stabilized and mark the recorder trace BEGIN SAMPLE/(DATE)/(TIME)/(INITIALS).

(43) Write the recorder chart speed on the strip chart.

(44) Dismantle the generator/bubble train set up.

2.4.2 Recorder Calibration

It is recommended that the recorder be calibrated at least twice a year. An accurate DC voltmeter (preferably a digital meter), a variable voltage source, and an accurate clock are required.

The recorder and the voltmeter are connected in parallel to the voltage source which is set at 0.000 volts. The recorder should be set on its normal operating range. The pen position is adjusted to 0 divisions on the strip chart (this may require internal adjustments). Next, the voltage source is set at 100% of the range for which the recorder is set, and

the pen adjusted to 100 divisions (by internal adjustment, if required). The two steps above are repeated until the proper zero and span response are obtained.

The pen response is next determined at 20, 40, 60, and 80 percent of full scale by adjusting the voltage source accordingly. If the linearity of these points is in excess of the manufacturer's specifications, servicing by a factory representative may be required.

The chart speed should be measured over a 24 hour period with an accurate clock. Again, if the recorder does not perform within specifications, factory servicing may be required.

The test results should be recorded in the calibration section of the log book.

2.4.3 Rotameter Calibration

Rotameters should be calibrated after cleaning (every six months) or at any sign of erratic behavior. Rotameters are normally used to measure ethylene plus sample flow in the analyser, the air flow rate in the ozone source, and the air flow rate in the HI sampling train. Ethylene flow is also indicated by a rotameter in some analysers. A calibration curve should be established for each rotameter to allow conversion of the flow meter indication to actual flow. Air can be used as the calibration fluid in all instances. The required equipment includes a wet test meter, bubblemeter, and manometer.

2.4.3.1 Calibrating Rotameters Against a Wet Test Meter

For the monitoring system as shown in Figure 6, the rotameters for monitoring the air flow rate through the O$_3$

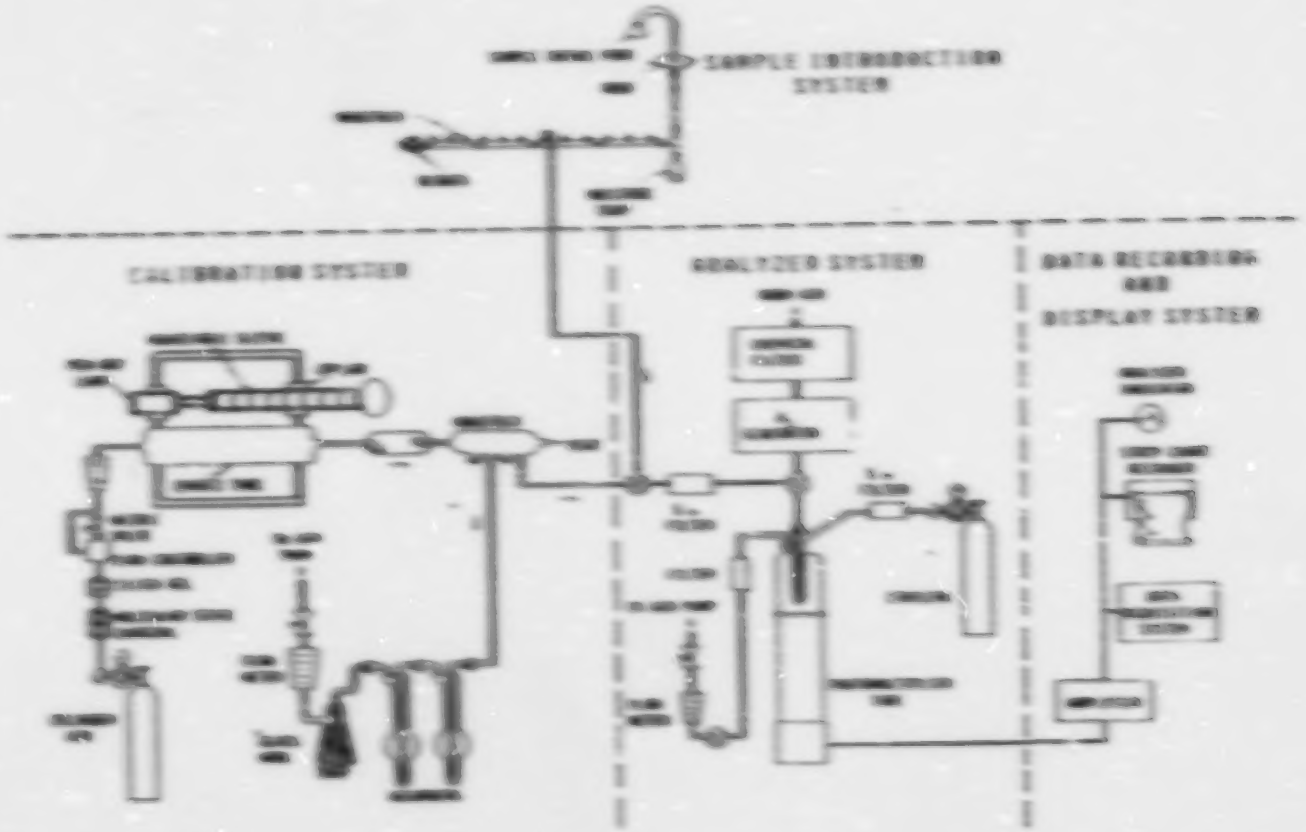

FIGURE 6

[illegible] MONITORING SYSTEM FLOW CHART

(Reference 5)

generator, the flow rate through the KI sampling train, and the sample air plus ethylene flow rate can be calibrated against a wet test meter using air as the calibration gas. Figure 7 shows a typical set up for calibrating rotameters under actual operating conditions. The two boxes labeled system apparatus represent system components used in the monitoring system. As an example, the rotameter in the KI sampling train could be calibrated with the apparatus connected as shown in Figure 8.

2.4.3.2 Procedure for Calibrating the KI Sampling Train/Sample Air Rotameter

The calibration is performed in the following manner:

(1) Set up the apparatus as shown in Figure 7*, making the connections as short as possible and of large enough inside diameter to avoid any appreciable pressure drops.

(2) Start the air flowing through the system and allow to flow for 5 to 10 minutes to allow the water in the wet test meter to reach saturation with the air.

(3) Before and after the complete calibration run, read and record room temperature and barometric pressure. Record average values on the calibration form in Figure 9. Use average values for subsequent calculations.

*To calibrate the sample air rotameter, connect the outlet side of the wet test meter upstream of the analyser.

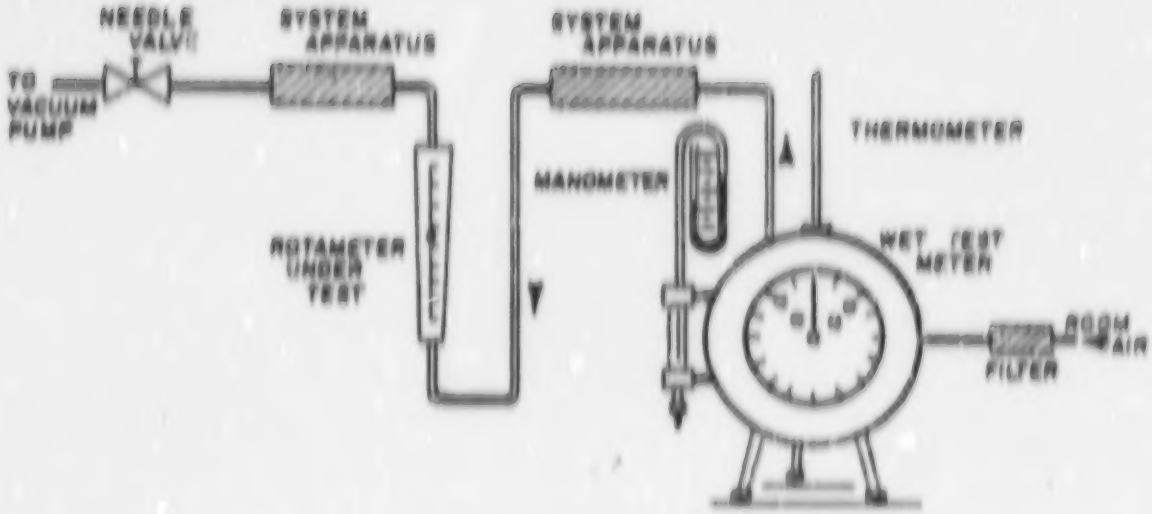

FIGURE 7
CALIBRATION ASSEMBLY USING WET TEST METER
(Reference 5)

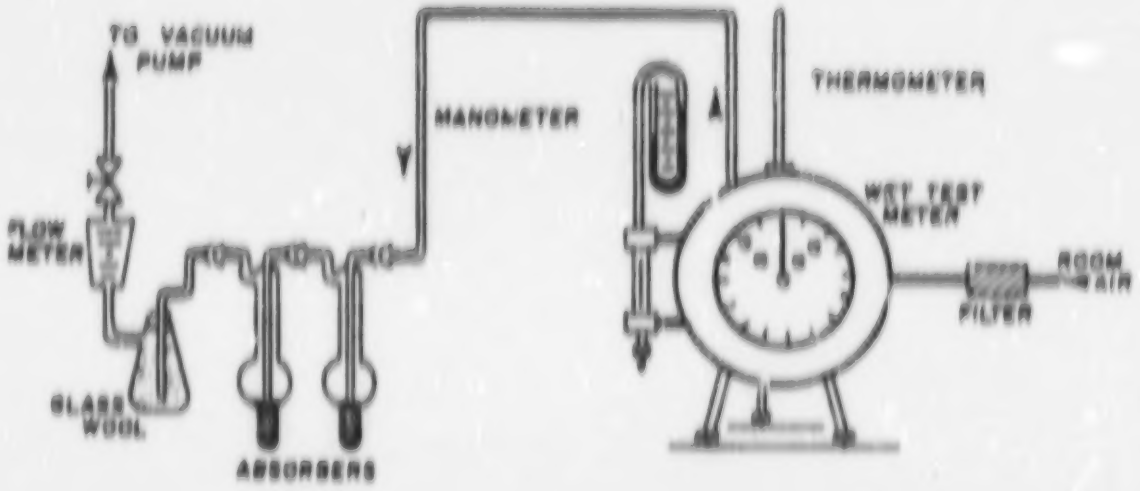

FIGURE 8
SETUP FOR CALIBRATION RI SAMPLING TRAIN
ROTAMETER UNDER OPERATIONAL CONDITIONS
(Reference 5)

(4) Adjust the needle valve to obtain a rotameter reading of about 20 percent of full scale.

(5) Take a pair of timed readings on the wet test meter (for best results use complete revolutions of the wet test meter), under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, total flow, elapsed time of run, manometer reading, and T_w (temperature of the liquid in the wet test meter) for each run on the calibration sheet of Figure 9.

(6) Convert all temperature and pressure readings to absolute units.

$°C + 273 = °K$

in $H_2O \times 1.87 = mm\ Hg$

(7) Calculate indicated flow rate readings for all recorded rotameter points by dividing the total flow by the elapsed time for that run.

(8) Using the following formula, convert these indicated flow rates to actual flow rates that would be indicated by

Analyser/Generator_____

Rotameter Serial No._____

Calibrated with_____

Location_____

Room Temperature (Average)_____°C

Atmospheric Pressure (Average)_____ mmHg

Calibrated By_____ Date_____

Test Point	Rotameter Reading	Total Flow l	Time min.	Flow rate l/min.	Manometer reading in H_2O	T_m
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						

FIGURE 9
ROTAMETER CALIBRATION DATA SHEET

the rotameter if it were calibrated for air at reference conditions of temperature and pressure.

$$Q_{RC} = Q_m \left(\frac{T_R}{T_m}\right)\left(\frac{P_m}{P_R}\right)$$

where:

Q_{RC} = flow rate at reference conditions (l/min),

Q_m = flow rate indicated by wet test meter (l/min),

T_R = reference temperature (298°K),

T_m = meter temperature (water temperature for wet test meter, usually same as room temperature) (°K),

P_R = reference pressure (760 mm Hg), and

P_m = barometric pressure minus the manometer reading (mm Hg). Note: For this set up the manometer reading should be very small (e.g., 0.1 to 0.2 in H_2O).

(9) Prepare a calibration curve of rotameter reading (y-axis) and flow rate at reference conditions (x-axis) by best fit to all points. It should be labeled "corrected for 25°C and 760 mm Hg". Figure 10 shows a typical rotameter calibration curve.

Analyzer/Generator_____ Corrected for ASF at
Flowmeter No._____ 25°C and 760 mmHg.
Location_____ Calibrated By_____

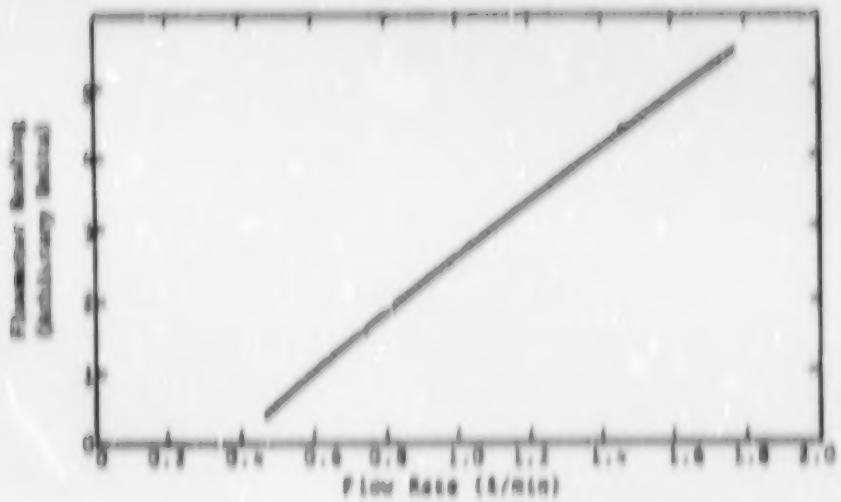

FIGURE 10
TYPICAL ROTAMETER CALIBRATION CURVE

2.4.3.3 Procedure for Calibrating the Rotameter in the O_3 Generator Circuit

The calibration is performed in the following manner:

(1) With the monitoring system connected as in Figure 6, disconnect the KI sampling train and the calibration line to the analyzer from the calibration manifold. Cap all calibration manifold outlets other than the one labeled "Vent" in Figure 6.

(2) Connect the vent of the calibration manifold to the inlet side of the wet test meter. Vent the outlet side of the wet test meter to the atmosphere.

(3) Start the air flowing through the system and allow to flow for 5 to 10 minutes to allow the water in the wet test meter to reach saturation with the air.

(4) Before and after the complete calibration run, read, and record room temperature and barometric pressure. Record average values on the calibration form in Figure 9. Use average values for subsequent calculations.

(5) Adjust the needle valve to obtain a rotameter reading of about 20 percent of full-scale.

(6) Take a pair of timed readings on the wet test meter (for best results use complete revolutions of the wet test meter), under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, total flow, elapsed time of run, manometer reading, and T_m (temperature of the liquid in the wet test meter) for each run on the calibration sheet of Figure 9.

(7) Convert all temperature and pressure readings to absolute units.

$°C + 273 = °K$

$in\ H_2O \times 1.87 = mm\ Hg$

(8) Calculate indicated flow-rate readings for all recorded rotameter points by dividing the total flow by the elapsed time for that run.

(9) Using the following formula, convert these indicated flow rates to actual flow rates that would be indicated by the rotameter if it were calibrated for dry air at reference conditions of temperature and pressure.

$$Q_{RC} = Q_m \left(\frac{T_R}{T_m}\right)\left(\frac{P_m}{P_r}\right)$$

where:

Q_{RC} = flow rate at reference conditions (ℓ/min),

Q_m = flow rate indicated by wet test meter (ℓ/min),

T_R = reference temperature (298°K),

T_m = meter temperature (water temperature for wet test meter, usually same as room temperature) (°K),

P_R = reference pressure (760 mm Hg), and

P_m = barometric pressure plus the manometer reading, minus the vapor pressure of the liquid used in the wet test meter at temperature T_m (mm Hg).

(10) Prepare a calibration curve of rotameter reading (y-axis) and flow rate at reference conditions (x-axis) by best fit to all points. It should be labeled "dry air at 25°C and 760 mm Hg". Figure 10 shows a typical rotameter calibration curve.

2.4.3.4 Calibration of the Ethylene Flow Rate Meter

The ethylene flow rate is approximately 25 cm^3/minute. Calibration at this low flow rate requires that a standard other than a wet test meter be used. A soap bubble meter is recommended. The same configuration as shown in Figure 7 can be used with a soap bubble meter replacing the wet test meter, provided a moisture trap is located between the bubble meter and system components.

Also, room air or compressed air can be used as the calibration gas. The flow rate error due to the difference in densities of air and ethylene is about one percent. The actual calibration procedure is the same as given in the above subsection with correction to reference conditions being made by the relationship in Step 9, with the exceptions that T_m becomes the room temperature and P_m is the barometric pressure.

2.4.4 Calibration of a Spectrophotometer for Wet Chemical Analysis of Ozone

The following apparatus is needed:

(1) Spectrophotometer with a 10 mm cuvette.

(2) Analytical balance.

(3) Deionized (DI) or distilled water and squeeze bottle.

(4) Disposable pipets.

(5) Plastic weighing trays.

(6) Two liters of fresh one percent neutral buffered KI absorber. This absorber should be prepared in boiled DI water and should be stored in a brown bottle. The solution should not be allowed to become warm.

(7) Primary standard grade arrenious oxide (As_2O_3).

(8) Drying over at 110°C.

(9) 1 M sodium hydroxide (NaOH).

(10) Stirring hotplate and magnetic stirbar.

(11) 1 M sulfuric acid (H_2SO_4).

(12) 100 ml volumetric flask.

(13) KI and resublimed iodine (I_2).

(14) Pan balance.

(15) 1:10 H_2SO_4.

(16) Sodium bicarbonate ($NaHCO_3$).

(17) 250, 100, and 50 ml beakers.

(18) 25, 20, 8, 6, 5, 4, 3, and 2 ml pipets.

(19) 50 ml buret, graduated in 0.1 ml.

(20) Five 50 ml volumetric flasks.

Procedure

(1) Turn on the spectrophotometer and set its wavelength at 352 nm.

(2) Dry about 20 grams of As_2O_3 in the oven at 110°C for one hour.

(3) Accurately weigh out 2.473 grams of As_2O_3. Transfer the As_2O_3 quantitatively to a 100 ml beaker. Add 25 ml of 1 N NaOH. Heat and swirl gently to dissolve all the As_2O_3.

(4) Add 25 ml of 1 N H_2SO_4. Transfer this solution quantitatively to a 1,000 ml volumetric flask. Rinse the insides of the beaker with DI water twice, and add

both rinses to the volumetric flask. Dilute to the mark with DI water and shake to obtain a homogeneous solution. This solution contains 0.050 N As_2O_3. Label the flask.

(5) Weigh out 4.0 grams of KI and 2.45 grams of resublimed I_2 on the pan balance. Quantitatively transfer these two solids to a 50 ml beaker. Add 10 ml DI water, and swirl until all the I_2 dissolves. Then quantitatively transfer this solution to a 500 ml volumetric flask, and dilute to the mark with DI water. Shake to obtain a homogeneous solution. This solution contains approximately the equivalent of 930 µg/ml O_2, but the solution must standardized.

(6) Accurately pipet 20 ml of the 0.050 N As_2O_3 solution into a 250 ml beaker. Add 10 drops of 1:10 H_2SO_4 with a disposable pipet.

(7) Add solid $NaHCO_3$ in small amounts until all bubble formation ceases. Then add 2 grams of $NaHCO_3$ in excess. Swirl to dissolve the $NaHCO_3$.

(8) Rinse the buret with the I_2 solution, and then fill the buret. Record the initial level of the solution in the buret.

(9) Add 3 ml of the starch solution to the As_2O_3 solution.

(10) Begin titrating the As_2O_3 solution with the I_2 solution. Swirl after each addition of the I_2 solution.

(11) When the blue I_2 starch color persists longer than two seconds after each addition, the end point is near. Add one ml of 1:10 H_2SO_4, and continue the titration until the blue color persists for at least 30 seconds while the beaker is being swirled. About 25 ml of I_2 solution is required.

(12) Record the number of ml of the I_2 solution required to titrate the As_2O_3 solution.

(13) Repeat Steps 6 though 12 to obtain a duplicate run.

(14) Compute the average number of ml required to titrate the As_2O_3 from the two runs.

(15) Determine the ug/ml O_3 in the I_2 solution by dividing 24,000 by the average ml of I_2 solution required for the titration. Record this ug/ml value and label the I_2 solution. This solution will be used to standardize the 1 percent NBKI solution.

(16) Pipet 5 ml of the standardized I_2 solution into a 500 ml volumetric flask, and dilute to the mark with 1% NBKI absorber. Shake to obtain a homogeneous solution, and label the flask. It contains 1% of the ug/ml O_3 in the standardized I_2 solution.

(17) Into five labeled, 50 ml volumetric flasks, pipet 2, 4, 6, 8, and 10 ml of the dilute I_2 solution. Dilute each to the mark with 1% NBKI absorber, using a disposable pipet to add the final few cc of absorber. Shake to obtain homogeneous solutions.

(18) Read the absorbances versus fresh 1% NBKI absorber. Use a 10 mm cuvette. Record the absorbances and the $\mu g/ml\ O_3$ values for each solution. The $\mu g/ml\ O_3$ values are 0.04, 0.08, 0.12, 0.16, and 0.20 times the value for the dilute I_2 solution.

(19) Turn off the spectrophotometer.

(20) Wash all dirty glassware with DI water.

(21) Plot absorbance versus $\mu g/ml\ O_3$. Draw the best straight line from origin through the points. Calculate the spectrophotometer factor B by picking a high absorbance point from the straight line and dividing the $\mu g/ml\ O_3$ value by the absorbance value. Record this factor to three significant figures and attach to the spectrophotometer.

2.9 Quality Assurance Audit Procedures

An essential part of a quality assurance program is testing the analyzer to determine how accurately it measures a test gas of known concentration. This information, along with the data processing check, helps to define the uncertainty associated with the routine monitoring results, and helps to detect problems in the monitoring system.

It is important that these control checks be performed without any non-routine adjustments or preparation of the system. They should be conducted by someone other than the routine operator. Advance notice of the audit should be kept to the minimum.

The frequency with which the control checks are performed will depend on whether the checks are done internally or by some outside group. The more frequently the control checks are performed, the better the confidence limits which can be assigned to the routine data. Costs also go up with frequency, so the actual number of checks will have to be determined by a trade-off between quality assurance goals and resources which can be dedicated to the quality assurance program. These considerations are discussed in detail in Reference 5, Pages 48-90, and can be used by management to plan an audit program.

The general procedure for performing a quality assurance audit is to introduce a known calibrated flow of ozone into the ambient sample line of the ozone analyser. The ozone analyser response is then compared to the known input, and the difference computed.

The ozone generator may be one already installed as part of the station, or it may be one dedicated solely to audit work. Most generators affect a change in ozone output by a change in the generator sleeve setting. Newer models are available that use varying current as a method of changing ozone output. The important point is that the generator output be calibrated at the time of the audit.

The neutral buffered KI bubbling procedure is the most widely used calibration technique. Other measures, such as gas phase titration or UV spectrophotometry, are satisfactory

alternatives to the NBKI method, and in the future may be more desirable. In the following discussion, it is assumed that the NBKI procedure is the calibration method used. The KI reagents used for auditing should be prepared and maintained separately from those reagents used in routine calibrations.

2.5.1 Audit Procedures

(1) Immediately upon arrival at the station, enter a record of your visit in the station and instrument log books. Include the date, time, purpose, and auditor's signature. Mark the strip chart record appropriately. Verify that the station analyzer has been operational for the previous 12 hours.

(2) If a generator is brought by the auditor, it should be turned on and allowed to stabilize. (If the generator requires a long time to stabilize, it is advisable to set up the generator the day before the audit.) Connect the generator air input to a suitable clean air source. Adjust the generator output flow to be in excess of the sum of the KI bubbling demand plus the ozone analyzer sample flow. An excess flow of about 50% is desirable.

(3) Adjust the generator sleeve setting to produce an ozone concentration that is in the range at which the station analyzer is operating.

(4) Connect the generator output to a suitable manifold and one port of the manifold to the station vent. Use glass or teflon only.

NOTE: If the station's ozone generator is used for the audit, disregard Steps 2 through 4. Instead, verify that the generator has been in operation long enough for the output to be stable. DO NOT ADJUST THE GENERATOR SETTINGS. The analyzer will be audited at the generator's output.

(5) Disconnect the analyzer sample line from the station manifold and connect to the generator manifold. Cap the sample manifold port.

(6) Plug in and turn on the spectrophotometer.

(7) Perform an NBKI calibration of the generator output as detailed in Section 2.4.1, Steps 14 through 28, with the following exceptions:

- Omit Step 17.

- Step 20 - omit recording the absorbance in the log book and on the data sheet shown in Figure 2.

The generator output determined by the NBKI calibration is the true ozone concentration, $(O_3\ ppm)_o$.

(8) Read the analyser response from the strip chart record. Convert the chart reading to ozone concentration (ppm) using the most recent analyser calibration curve or conversion table (see Figure 4) found in the instrument log book. Label this value $(O_3\ ppm)_m$.

(9) Compute the relative error, d_i (%), between the true and measured ozone values:

$$d_i = \frac{(O_3\ ppm)_m - (O_3\ ppm)_s}{(O_3\ ppm)_s} \times 100$$

(10) Reconnect the analyser ambient sample line to the station manifold.

(11) Return the station to its normal configuration.

(12) Forward the results of the audit to the appropriate supervisory personnel.

3.0 QUALITY ASSURANCE PROGRAM FOR MONITORING CO

3.1 Selection of CO Monitoring Equipment

The Federal Reference Method for monitoring CO is the non-dispersive infrared technique (NDIR). Minimum performance requirements for NDIR analyzers are described below:

A. Range - 0-50 ppm

B. Output (minimum) - 0-10, 100, 1000, 5000 MV full scale

C. Minimum detectable sensitivity - 0.5

D. Lag time - 15 seconds

E. Time to 90 percent (maximum) - 15 seconds

F. Rise time, 90 percent (maximum) - 15 seconds

G. Fall time, 90 percent (maximum) - 15 seconds

H. Zero drift (maximum) - 3 percent/week, not to exceed ± percent/24 hours

I. Span drift (maximum) - 3 percent/week, not to exceed 1 percent/24 hours

J. Precision (minimum) - ±0.5 percent

K. Noise (maximum) - ±0.5 percent

L. Interference equivalent (maximum) - 1 percent of full scale

M. Operating temperature range (maximum) 20-30°C

N. Operating humidity range (minimum) - 10-100 percent

O. Linearity (maximum deviation) - 1 percent full scale

These requirements for NDIR analaysers are in the performance specifications outlined in the Federal Register, Volume 36, No. 84, Part II, Friday, April 30, 1971.

3.2 Site Selection and Installation of Equipment

A detailed discussion of general monitor siting requirements is contained in Reference 3. Four basic types of CO monitoring sites are identified:

- Street canyon (peak or average)
- Neighborhood (peak or average)
- Corridor
- Background

The major source of CO emissions is vehicular. Because of the great variability in traffic patterns, both spatially and temporally, CO concentrations vary widely as a function of space and time. Selection of a particular site depends on the specific monitoring goal(s) and the type of site described above. General siting guidelines are offered in Table 1. For more detailed discussions on siting guidelines, the reader should refer to the most recent EPA guideline series documents.

Any CO monitoring station will consist of a sample introduction system, the analyzer system and a data recording and

Table 1

[redacted]

(Reference 3)

Site Type	Height Above Ground	Expected Concentration Gradient with Height (1-hr Average)	Separation of Receptor from Influencing Sources		General Remarks
Street Canyon					
Peak Conc.	3 ± ½ m	~.5 ppm/m	Mid-sidewalk or 3m from side of building in leeward side of street.		Central business District. High density slow moving traffic. Dense multiple story buildings lining both sides of street. >30 m from intersection
Average Conc.	3 ± ½ m	.3 ppm/m	Mid-sidewalk or 2 m from side of building.		
Neighborhood			Setback	VPD	Commercial or residential neighborhood. This separation criteria limits the effect of these screens to ~1 ppm.
Peak Conc.	3 ± ½ m	5%/m	3.5 m	100,000	
Average Conc.	3 ± ½ m	5%/m	1.5 m	50,000	
			300 m	10,000	
			100 m	5,000	
			2> m	1,000	
			25 m	any	
Corridor	3 ± ½ m	< .3 ppm/m > 5%/m	Dependent on traffic volume, road configuration and setback distance of commercial or residential activity		Stop and go or limited access traffic > 50,000 VPD or greatest in area.

Table 1 (Cont.)

SPECIFIC PAMS EXPOSURE CRITERIA

Site Type	Height Above Ground	Expected Concentration Gradient With Height (1-hr Average)	Separation of Monitor from Influencing Sources	General Remarks
Background	3 to 10 m	.25/m	5 to 6 km; > 3000 VPH max 400 m; > 100 VPH	35 km downwind in least frequent wind direction from city, limit effects to .2 ppm.
New Source Review				
Preconstruction	3 ± ½ m	50/m	Usually the same as neighborhood	Area of lowest concentration is proposed indirect source location for background
Post-Construction	3 ± ½ m	> 50/m to < .5 ppm		Area of maximum concentration in area of complete area source.

display system. A typical monitoring system flow chart is shown in Figure 11. The monitor housing should provide a stable temperature environment, and a voltage-regulated power supply. Because NDIR instruments are sensitive to vibrations, care must be exercised to isolate the unit as much as possible from vibrations.

Specific analyzer installation and start-up procedures may differ, depending on the particular manufacturer. In general, a source of zero air, the span gas, and the ambient sample line must be connected to the analyzer. A vent line is also needed. (A sample pump bypass line is needed in many installations.) Care must be exercised to insure that the vent line port is at ambient pressure so that no vacuum or pressure occurs in the sample chamber during sampling. It is also recommended that the zero and span cylinders be connected to the analyzer with the connecting line(s) vented to ambient. During zero or span operations, an excess flow is maintained. This procedure prevents pressurization (or creation of a vacuum) during zero/span operations, and insures that the zero/span/ambient sampling all occur at the same analyzer inlet pressure and flow rate.

Following proper installation, the monitor should undergo a routine start-up and check-out operation. These procedures may vary somewhat, depending on the specific instrument and installation configuration. It should consist of at least the following operations:

(1) Turn the analyzer and flow pump ON. Observe that the POWER indicator is on, and the sample pump is running, and the mode switch is on SAMPLE. Set the range control to 50 ppm*.

*It is assumed throughout that the monitor will be operated on the 0-50 ppm range (The EPA Reference Method, Reference 1).

(2) Adjust the FLOW ADJUST valve to obtain the desired sample flow rate. Most instruments offer a fairly wide flow rate range that gives satisfactory performance. The selected flow rate will depend on the desired analyser response time (the faster the flow, the shorter the response time).

(3) Verify that the proper electrical connections are made to the data recording system.

(4) Place the mode selector switch to ZERO. Adjust the zero air cylinder second stage regulator to obtain the same flow rate (as indicated by the instrument rotameter) as in the SAMPLE mode. Make certain the zero air vent line has a positive flow.

NOTE: Because the NDIR is sensitive to temperature changes, it is important that the zero and span cylinders be at the station temperature before introducing their gases into the analyser.

(5) After the analyser response has stabilised, adjust the ZERO ADJUST control to obtain a zero meter reading. Lock the control. Continue the zero reading for about three hours to observe any drift.

(6) Put the mode switch in the SPAN position. Wait for the response to stabilise, then adjust the SPAN ADJUST control to obtain an

instrument response equal to the concentration of the span gas. Operate on SPAN for three hours to observe any drift.

(7) Perform a flow rate sensitivity check as described below.

(8) Return the mode switch to SAMPLE. Shut off the ZERO and SPAN cylinders.

3.2.1 Flow Rate Sensitivity Check

For analyzers with a pressurized cell, the following procedure is used:

(1) With the analyzer in normal operating condition, connect a span gas with a concentration corresponding to approximately 80 percent of full scale to the analyzer.

(2) Adjust the sample flow and sample cell pressure to the normal operating values and allow time to obtain a stable trace.

(3) Mark the trace with flow rate and cell pressure values.

(4) Adjust the flow rate to one-half of its previous value. Do not readjust the sample cell pressure. Allow time to obtain a stable trace.

(5) Mark the trace with flow rate and cell pressure.

(6) Adjust the flow rate to three times its present setting. Allow time to obtain a stable trace.

(7) Mark the trace with flow rate and cell pressure.

Record all results in the calibration section of the log book, and also forward the results to the supervisor.

For analysers with non-pressurised cells, the following procedure should be used:

(1) With the analyser in normal operating condition, connect a span gas with a concentration corresponding to approximately 80 percent of full scale to the analyser.

(2) Adjust the sample flow to the normal operating value and allow time to obtain a stable trace.

(3) Mark the trace with flow rate.

(4) Adjust the flow to 80 percent of the normal value and allow time to obtain a stable trace.

(5) Mark the trace flow rate.

(6) Repeat (4) and (5) for flows of 90, 100, 110, and 120% of normal.

(f) Record all results in the calibration section of the log book, and also forward the results to the supervisor.

3.3 Routine Operation Procedures

It is assumed that the instrument is operating properly and a technician trained in the operation of the NDIR is carrying out the routine procedures.

NOTE: The following procedures assume that the analyser has a ZERO/SPAN/SAMPLE mode selector switch to change from zero gas to span gas to ambient. References to changing the mode switch to a particular setting would not apply to analysers having no switching capability. For the latter type analysers, the instructions to "change the mode switch" should be read to mean connect the appropriate gas flow to the analyser. Also, some analysers do not have a pressurised cell. In such an instance, references to pressurised cells should be ignored.

(1) Make an entry in the station log book noting the date, time and purpose of your visit.

(2) Record the analyser unadjusted zero and span control settings in the log book and on the strip chart. If they are different from the previously recorded settings, notify the supervisor. Note the discrepancy in the log book and on the strip charts.

(3) Record the unadjusted sample flow rate in the log book and on the daily check sheet (see Figure 12 for example). Check the cell pressure if the analyser has a pressurised cell. Record as above.

[illegible] ANALYZER DAILY CHECK SHEET

Station Name _____ Location _____

Analyzer Number _____

Date	Operator	Sample Flow Rate (L/min)		Sample Cell Pressure (lbf^{-2})		Ozonator Pressure/(lbf^{-2})		Mass Control Knob Setting		Readjusted Calibration	
		Initial	Final	Initial	Final	Zero	Span	Zero	Span	Zero	Span

FIGURE 12

SAMPLE DAILY CHECK SHEET

[Reference 6]

(4) Check the zero and span cylinder high side pressures. Record these in the log book. Cylinders should be replaced when the main pressure is less than 100 psig. DO NOT REPLACE AT THIS TIME.

(5) Check the shelter temperature record. If temperatures outside the allowable operating range are observed, note such on the strip chart and notify the supervisor.

(6) Verify that the zero and span cylinder pressures are properly set and record on the daily data sheet.

(7) Put the analyzer mode switch in the SPAN mode. If necessary, adjust the flow rate so that it is the same as the SAMPLE flow rate. Allow the response to stabilize to CO ppm and record the unadjusted span reading in the log and on the daily check sheet. Label the strip chart unadjusted span.

(8) Put the analyzer mode switch on ZERO. If necessary, adjust the flow rate until it is the same as the SAMPLE flow rate. Wait until the response has stabilized. Record the unadjusted zero reading and label the strip chart as above.

(9) Compute the percent drift in the zero and the span responses from the last adjusted zero (span) and the current, unadjusted zero (span).

$$\text{Percent Drift} = \frac{\text{Unadjusted Response (ppm)} - \text{Adjusted Response (ppm)}}{\text{Adjusted Response (ppm)}} \times 100$$

If the drift exceeds acceptable limits established by the Quality Assurance Program Manager, make a notation on the strip chart and notify the supervisor.

(10) Perform all necessary system checks, station repairs, and instrument maintenance. This would include all regularly scheduled maintenance, cylinder replacement, water vapor control check, filter replacement, and sampling system checkout and cleaning (if necessary). If the span cylinder is replaced, the concentration of the new assayed span cylinder must be entered in the log book and used in future span checks. The span response of the new cylinder should be checked. Also, check the data recording system and perform any scheduled calibration or maintenance such as paper change, refilling ink supply, cleaning pen, etc. Examine the ambient data record for evidence of system malfunction. Evidence of malfunction could include:

- A straight trace for several hours (other than minimum detectable).

- Excess noise as indicated by a wide solid trace, or erratic behavior such as spikes that are sharper than is possible with the normal instrument response time. Noisy outputs usually result when analyzers are exposed to vibration sources.

- A long steady increase or decrease in deflection.

- A cyclic pattern of the trace with a definite time period indicating a sensitivity to changes in temperature or parameters other than CO concentration.

- Periods where the trace drops below the zero baseline. This may result from a larger than normal drop in the ambient room temperature or power line voltage.

If any of the above conditions are detected, data should be flagged, troubleshooting done, and the supervisor informed. Data should be declared invalid only if malfunction of the instrument is detected; otherwise, it should be reported. Note all observations in the log book.

(11) Put the analyzer mode switch on ZERO. If necessary, adjust the flow rate to the SAMPLE flow rate. Wait for the response to stabilize. Then adjust the ZERO ADJUST control to obtain the proper zero response on the analyzer concentration meter. Adjust the recorder zero adjust to obtain a five percent chart reading. (If the recorder chart has an offset zero, adjust to this line.) Label the strip chart adjusted zero and enter the new zero control setting in the log and on the daily check sheet.

(12) Put the mode switch on SPAN. Adjust the flow, if necessary, to the SAMPLE flow rate. Wait until the response stabilizes.

Label the strip chart adjusted span and record the span setting and adjusted span ppm in the log and on the daily check sheet.

(13) Put the mode switch on SAMPLE. Wait for the response to stabilize. Adjust the sample flow rate, if necessary, and record the final sample flow and cell pressure in the log and on the daily check sheet. Label the chart BEGIN AMBIENT. Note the chart speed, date, and time on the chart.

(14) Turn off the valves on the zero and span cylinders.

3.3.1 Particulate Filter Check

A filter with a porosity of two to ten micrometers is used to keep large particles from reaching the sample cell.

With no filter in the system, observe the sample flow rate. Place a clean filter in the filter holder and read the new flow rate. Note any drop in flow rate due to the clean filter. Record the magnitude of the drop in the maintenance log book.

Initially measure the flow rate with and without the "dirty" filter once a month. Replace the filter if the flow rate drop for the dirty filter, divided by the drop caused by the clean filter, is more than two. Experience will suggest how often such checks need to be made for a given site.

3.4 Routine Calibration Procedures

It is essential to any quality assurance program that accurate, reliable calibration standards be maintained. Data

quality can be no better than the quality of the calibration standards. A zero gas containing less than 0.1 mg CO per cubic meter (~90 ppb) should serve as a satisfactory zero level gas. Span gases corresponding to 10, 20, 40, and 80 percent full scale (on 50 ppm range) are also needed.

The National Bureau of Standards supplies standard gases of CO in N_2 in wax-lined cylinders. NBS standards are certified for one year. For NDIR work, CO in air is the preferred standard. These are available commercially. It is necessary, however, that the commercial cylinders be calibrated against an NBS standard cylinder. Procedures for standardizing commercial cylinders against an NBS standard are given in Appendix II.

Multi-point calibrations are required when:

(1) The analyzer is first purchased and prior to ambient sampling.

(2) Periodically (monthly) during any extended sampling program.

(3) Whenever maintenance is performed that could change the response characteristics.

(4) When audit results indicate unsatisfactory performance.

Detailed calibration procedures are given by each instrument manufacturer and should be followed in calibrating a specific brand analyzer. A general calibration procedure is documented below which incorporates the aspects of good quality assurance practices.

3.4.1 NDIR Multi-Point Calibration

NOTE: If the calibration is being performed on an operational analyser that is collecting ambient data, an UN-ADJUSTED ZERO/SPAN (Section 3.3) must be performed before the calibration is done.

(1) Verify that the power is on and the analyser has stable response. (If the analyser was just turned on, stabilization usually requires several hours depending on the individual analyser.)

(2) Connect zero gas to the analyser.

(3) Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure. Caution: Do not exceed the pressure limit of the sample cell.

(4) Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling.

(5) Let the zero gas flow long enough to establish a stable trace. Allow at least five minutes for the analyser to stabilize.

(6) Adjust the analyser zero control knob to obtain a zero meter reading. Adjust the recorder zero adjust control until the trace corresponds to the line representing

five percent of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

(7) Let the zero gas flow long enough to establish a stable trace. Allow at least five minutes for this. Mark the strip chart trace as adjusted zero.

(8) Disconnect the zero gas.

(9) Connect the span gas with a concentration corresponding to approximately 80 percent full scale.

(10) Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

(11) Set the sample flow rate, as read by the rotameter, to the valve that is to be used during sampling.

(12) Let the span gas flow until the analyzer stabilizes.

(13) Adjust the span control until the deflection corresponds to the correct percentage of chart as computed by:

$\frac{C_s \text{ (ppm)}}{C_f \text{ (ppm)}} \times 100 \div 5$ (% Zero Offset) = Correct Percentage of Chart

where

C_s = Concentration of span gas in ppm, and

C_f = Full scale reading of analyser in ppm.

As an example, the correct percentage of chart for a span gas of 40 ppm would be

$\frac{40 \text{ ppm}}{50 \text{ ppm}} \times 100 \div 5 = 85$

(14) Allow the span gas to flow until a stable trace is observed. Allow at least five minutes. Mark the strip chart trace as adjusted span and give concentration of span gas in ppm.

(15) Disconnect the span gas.

(16) Repeat Procedures 2 through 8 and

- If no readjustment is required, go to Procedure 17.
- If a readjustment greater than 1 ppm is required, repeat Procedures 9 through 16.

(17) Lock the zero and span controls.

(18) Connect the calibration gas with a concentration corresponding to approximately

ten percent full scale to the analyser.

(19) Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

(20) Set the sample flow rate to the value used during sampling.

(21) Let the calibration gas flow until the strip chart trace stabilizes. Note: No adjustments are made at this point.

(22) Disconnect the calibration gas.

(23) Repeat Procedures 18 through 22 for each of the calibration gases with concentrations corresponding to approximately 20 and 40 percent of full scale in that order.

(24) Fill in the information required on a calibration sheet and construct a calibration curve of deflection as percent of chart versus concentration in ppm as illustrated in Figure 13. Draw a best fit, smooth curve passing through the zero and span points and minimizing the deviation of the three remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should be either a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying

Location_____Date_____Operator_____

Analyzer No._____Range_____Flow Rate_____Cell Pressure _____

Zero Gas_____. Cylinder Pressure_____Cylinder No._____

Upscale gas (80%)_____ Cylinder Pressure_____Cylinder No._____
(10%)_____ Cylinder Pressure_____Cylinder No._____
(20%)_____ Cylinder Pressure_____Cylinder No._____
(40%)_____ Cylinder Pressure_____Cylinder No._____

Zero Control Setting_____Span Control Setting_____

Recorder Type _____Serial No. _____

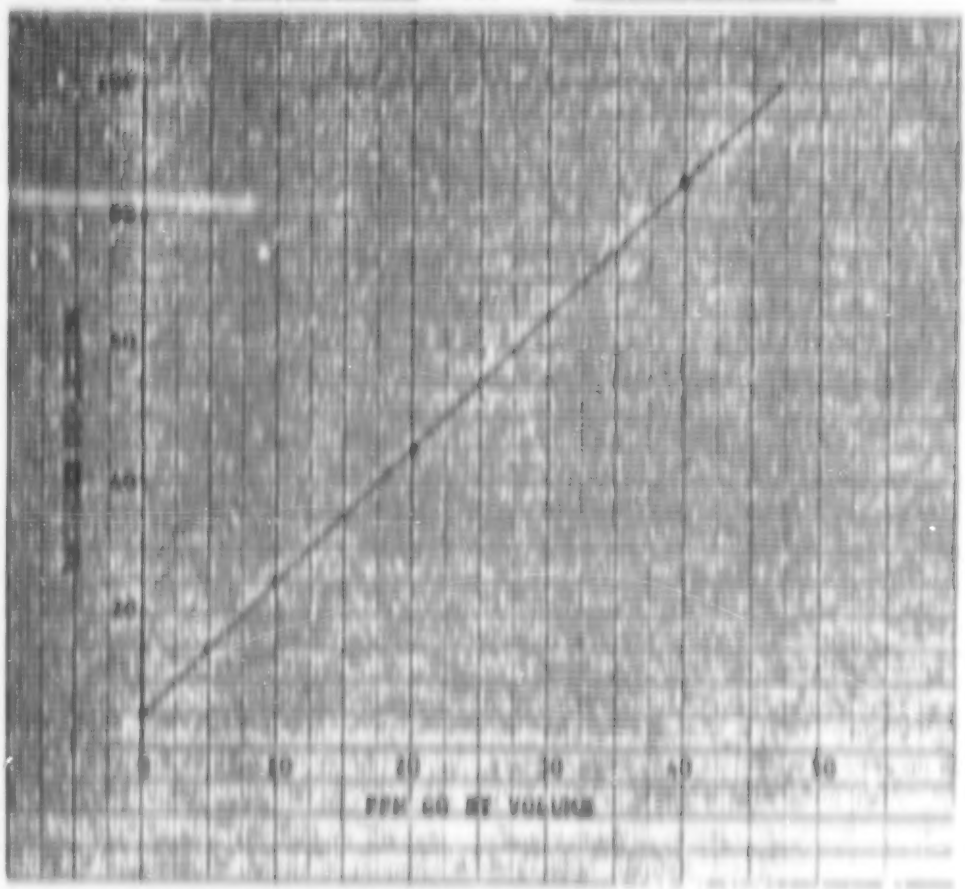

FIGURE 11
SAMPLE CALIBRATION CURVE
(Reference 6)

appropriate constraints to force the curve through the zero and span points. This procedure becomes quite involved, however; and the most frequently used technique is to fit the curve by eye.

(25) Recheck any calibration point deviating more than ± (1.0 + 0.02 C_C) ppm from the smooth calibration curve. (C_C is the concentration from the curve for the same recorder response as the data point.) If the recheck gives the same results, have that calibration gas re-analysed. Use the best fit curve as the calibration curve.

(26) Fill in the calibration conversion sheet (see Figure 14) from the calibration curve.

(27) In certain situations, the supervisor may request that the calibration be repeated (replicated). In this case, obtain both sets of data and follow his instructions for preparing a calibration curve.

(28) Return the analyser to the SAMPLE mode. Adjust the sample flow rate to the proper value, if necessary.

3.4.2 Recorder Calibration

It is recommended that the recorder be calibrated at least twice a year. An accurate DC voltmeter (preferably a digital meter), a variable voltage source, and an accurate clock are required.

Analyzer No. _____ Date of Calibration _____

% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM
0.0		30.5		60.5		90.5		90.5	
0.5		31.0		61.0		91.0		91.0	
1.0		31.5		61.5		91.5		91.5	
1.5		32.0		62.0		92.0		92.0	
2.0		32.5		62.5		92.5		92.5	
2.5		33.0		63.0		93.0		93.0	
3.0		33.5		63.5		93.5		93.5	
3.5		34.0		64.0		94.0		94.0	
4.0		34.5		64.5		94.5		94.5	
4.5		35.0		65.0		95.0			
5.0									
5.5		35.5		65.5		95.5		95.5	
6.0		36.0		66.0		96.0		96.0	
6.5		36.5		66.5		96.5		96.5	
7.0		37.0		67.0		97.0		97.0	
7.5		37.5		67.5		97.5		97.5	
8.0		38.0		68.0		98.0		98.0	
8.5		38.5		68.5		98.5		98.5	
9.0		39.0		69.0		99.0		99.0	
9.5		39.5		69.5		99.5		99.5	
10.0		40.0		70.0		100.0		100.0	
10.5		40.5		70.5		100.5			
11.0		41.0		71.0					
11.5		41.5		71.5					
12.0		42.0		72.0					
12.5		42.5		72.5					
13.0		43.0		73.0					
13.5		43.5		73.5					
14.0		44.0		74.0					
14.5		44.5		74.5					
15.0		45.0		75.0					
15.5		45.5		75.5					
16.0		46.0		76.0					
16.5		46.5		76.5					
17.0		47.0		77.0					
17.5		47.5		77.5					
18.0		48.0		78.0					
18.5		48.5		78.5					
19.0		49.0		79.0					
19.5		49.5		79.5					
20.0		50.0		80.0					

FIGURE 14

TABLE FOR CONVERTING TRACE DEFLECTION IN PERCENT OF CHART TO CONCENTRATION IN PPM

(Reference 6)

The recorder and the voltmeter are connected to the voltage source which is set at 0.000 volts. The recorder should be set on its normal operating range. The pen position is adjusted to 0 divisions on the strip chart (this may require internal adjustments). Next, the voltage source is set at 100 percent of the range for which the recorder is set, and the pen adjusted to 100 divisions (by internal adjustment, if required). The two steps above are repeated until the proper zero and span response are obtained.

The pen response is next determined at 20, 40, 60, and 80 percent of full scale. If the nonlinearity of these points is in excess of the manufacturer's specifications, servicing by a factory representative may be required.

The chart speed should be measured over a 24 hour period with an accurate clock. Again, if the recorder does not perform within specifications, factory servicing may be required.

3.4.3 Flow Meter Calibration

Rotameters usually require cleaning every six months to a year. It is suggested that they be calibrated after having been cleaned or at any sign of erratic behavior. Calibration can be accomplished using a wet test meter as a secondary standard or a rotameter which has been recently calibrated against a secondary standard.

The easiest method is to use a calibrated rotameter as follows*:

*See Section 2.4 for calibration by a wet test meter.

(1) Place the calibrated rotameter in series with the rotameter to be calibrated and adjust the flow rate as read on the calibrated rotameter to 80 percent of full scale.

(2) Adjust, if necessary, the test rotameter until it reads the same as the calibrated rotameter and lock the adjustment screw or knob.

(3) Work down scale stopping at 65, 50, 35, 20, and 5 percent of full scale. Record corresponding readings from both rotameters on a rotameter calibration sheet.

(4) Using the calibration curve for the calibrated rotameter, construct a calibration curve of rotameter reading versus flow rate for the test rotameter.

It is suggested that initially the sample cell pressure gauge be calibrated at six month intervals or at any sign of erratic behavior of the gauge, such as a change larger than 1 psi in the sample cell pressure during a sampling period in which the sample flow rate did not change by more than 0.5 ft^3/hr. If after two six-month calibrations the gauge shows no sign of change (i.e., reads within 1 psi of the calculated pressure), go to once a year calibrations. Repeat the process making the period shorter or longer according to the magnitude of change of the gauge until an optimum calibration interval is realised.

3.5 Quality Assurance Audit Procedures

An essential part of a quality assurance program is random testing of the analyzer to determine how accurately it measures a test gas of known concentration. This information, along with the data processing check, helps to define the uncertainty associated with the routine monitoring results and helps to detect problems in the monitoring system.

It is important that these control checks be performed without any non-routine adjustments or preparation of the system. It is desirable that they be conducted by someone other than the routine operator.

The frequency with which the control checks can be performed will probably depend on whether the checks are done internally or by some outside group. The more frequently the control checks are performed, the better the confidence limits which can be assigned to the routine data. Costs also go up with frequency, so the actual number of checks will have to be determined by a trade-off between quality assurance goals and resources which can be dedicated to the quality assurance program. These considerations are discussed in detail in Reference 6, Pages 50-103, and can be used to plan an audit program.

3.5.1 Audit Procedures

(1) Verify that the analyzer is operational and the response is stable.

(2) Disconnect the ambient sample line from the ambient manifold. Cap the manifold port.

(3) Connect the ambient sample line to one side of a three-way tee connector. Connect one side of the tee to the cylinder. The remaining side of the tee is connected to a vent port.

NOTE: The audit cylinder temperature should be allowed to stabilize to the station temperature.

(4) Open the cylinder valve and adjust the second stage regulator to obtain an analyzer flow equal to the normal sample flow. Verify that a positive flow is maintained at the vent port.

(5) If necessary, adjust the analyzer flow rate to the ambient sample flow rate.

(6) Allow the instrument response to stabilize to the audit flow. Note on the strip chart record the audit cylinder number and the concentration of the cylinder. Take a five minute reading.

(7) Convert the chart deflection to ppm using the most recent calibration conversion table (Figure 14).

(8) Compute the relative error between the known input $(CO\ ppm)_a$, and the measured concentration $(CO\ ppm)_m$.

$$\text{Relative Error (\%)} = \frac{(CO\ ppm)_a - (CO\ ppm)_m}{(CO\ ppm)_a} \times 100$$

(9) Disconnect the ambient sample line from the audit cylinder after closing the cylinder valve. Reconnect the ambient line to the station manifold.

(10) Enter a record of the results in the instrument or station log book.

(11) Give copies of the audit results to the station operator and quality assurance supervisor.

3.5.2 Water Vapor Interference Check

Water vapor checks should be independent and random; that is, a qualified individual other than the regular operator should make the check. Also, the regular operator should not know in advance when the check is to be made. The individual making the check should not adjust, replace, or in any way change the water vapor control unit before performing the check. The exact procedure for performing the check will depend on the type of control being used. Two procedures are given below (Reference 6).

Drying Agent - When a scrubber column filled with a drying agent is used to control water vapor interference, the check can be performed in the following manner:

(1) Connect the dry zero gas directly to the analyzer inlet, bypassing the scrubber column. Let the zero gas flow until a stable trace is obtained. Mark the trace as dry zero gas.

(2) Remove the segment of line bypassing the drying agent. Place a 50 ml impinger containing 25 ml of distilled water, at room temperature, in the sample line such that the zero gas passes through the impinger, drying agent, and analyzer in that order. Caution: With NDIR analyzers having a pressurized cell, this impinger may have to be pressurized. If so, it will have the full cell or pump pressure and will be subject to explosion. Use a pressure vessel of adequate pressure capacity, and avoid the use of glass, if possible.

Let the gas flow until a stable trace is obtained. Mark the trace as response to saturated zero gas.

(3) Determine the difference in the two traces as an equivalent CO concentration in ppm. Always subtract the dry measurement from the saturated measurement. In some cases, negative values will result due to normal measurement error. Document the check in the instrument log book and give a copy of the results to the supervisor.

Other Methods - Other methods includn refrigeration, refrigeration preceded by humidifier, filter cells, or optical filters. When refrigeration alone is used, the cold trap should be thoroughly drained before the test and the dry zero gas allowed to flow at least 10 minutes before reading. Otherwise, all these methods can be checked in the following manner:

(1) Pass zero gas through the system in the same manner as is done in zero and span calibrations. Mark the trace as dry zero gas.

(2) Insert a 50 ml impinger filled with 25 ml of distilled water at room temperature into the sample inlet line on the inlet side of the water control unit. Caution: With NDIR analyzers having a pressurized cell, this impinger may have to be pressurized. If so, it will have the full cell or pump pressure and will be subject to explosion. Use a pressure vessel of adequate pressure capacity and avoid the use of glass, if possible.

(3) Pass the zero gas through the impinger and system and mark the trace as saturated zero gas.

(4) Determine the apparent change in concentration in ppm by subtracting the response to dry gas from the response to saturated gas.

(5) Allowable interference levels for different control methods should be specified by the supervisor from method specifications or from the desired accuracy of the reported data. If the interference exceeds acceptable limits, appropriate corrective action is necessary.

4.0 RECORD KEEPING PROCEDURES

Record keeping is an important aspect of any quality assurance program. Adequate documentation is needed to substantiate or invalidate ambient data and assure data integrity. The need for documentation cannot be overstated. Any action or observation connected with the collection of ambient air quality data should be fully documented. Instrument accuracy becomes a moot point if records cannot be produced to substantiate such claim. To produce reliable, defendable data, documentation should include daily operations, preventive and corrective maintenance, calibrations, quality assurance audits, general conditions, and unusual occurences.

Every monitoring site should have a station log book. An entry should be made every time the station is visited noting the date, time, visitor, and purpose. Also, observations of the station and surrounding conditions should be recorded if they relate to data integrity. For example, local conditions may include nearby construction that could affect ambient conditions. Any malfunctions in the station operation should be recorded. This might include such things as power failures, temperature control problems, instrument malfunctions, etc. Instrument changes or cylinder replacement should also be recorded.

In addition to the station log, each instrument should have a log which includes a section for routine operations, calibrations, and maintenance. The routine operation section should include all zero/span data, flow rate measurements, and instrument control setting data. The calibration section should contain all instrument calibration data as well as calibration standards information. Finally, a record of instrument maintenance should be kept. This should include any repairs to the instrument, filter replacements, etc.

5.0 DATA REDUCTION AND DATA HANDLING

Routine data processing may be performed by the instrument operator or preferably by some other person. It is helpful to have a sheet such as the one in Figure 15 made up to use in reduction of the strip chart data. (The columns labeled "check" are for use in auditing the data processing and left blank during routine data processing.)

The basic procedure is described below (Reference 6):

(1) Obtain the strip chart record for the sampling period in question. The record must have adjusted span and zero traces at the beginning of the sampling period and unadjusted span and zero traces at the end of the sampling period.

(2) Fill in the identification data called for at the top of an hourly averages sheet (see Figure 15).

(3) Using a straight edge, draw a straight line from the adjusted zero at the start of the sampling period to the unadjusted zero at the end of the sampling period. This line represents the zero baseline to be used for the sampling period.

(4) Read the zero baseline in percent of chart at the midpoint of each hour interval and record the value on the hourly averages sheet.

CITY_____ SITE NUMBER_____

SITE LOCATION_____ POLLUTANT_____

DATE_____ OPERATOR_____

CHECKED_____

Hour	Replicate									
	Original	Check	Original	Check	Original	Check	Original	Check	Original	Check
0-1										
1-2										
2-3										
3-4										
4-5										
5-6										
6-7										
7-8										
8-9										
9-10										
10-11										
11-12										
12-13										
13-14										
14-15										
15-16										
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19-20										
20-21										
21-22										
22-23										
23-24										

FIGURE 13
SAMPLE SHEET FOR RECORDING HOURLY AVERAGES
(Reference 6)

(5) Determine the hourly averages by using a transparent object, such as a piece of clear plastic, with a straight edge at least one inch long. Place the straight edge parallel to the horizontal chart division lines. For the interval of interest between two vertical hour lines, adjust the straight edge between the lowest and highest points of the trace in that interval, keeping the straight edge parallel to the chart division lines, until the total area above the straight edge bounded by the trace equals the total area below the straight edge bounded by the trace and hour line.

Read and record on the hourly average sheet the percentage of chart deflection.

Repeat the above procedure for all the hour intervals for which the analyser was sampling and which have not been marked invalid. Record all values on the hourly averages sheet in the column headed Reading under "Original".

(6) Subtract the zero baseline value (Column 2) from the reading value (Column 1) and record the difference in Colum 3.

(7) Add the percent zero offset (Column 4) to the difference.

(8) Convert percentage chart values to concentration in ppm using the current calibration conversion

tables developed from the calibration curve. Record the ppm values in Column 5 on the hourly averages sheet.

(9) Transcribe the data from the hourly averages sheet to a SAROAD hourly data form. This procedure is described on Pages 32-35 of Reference 6. Further information is available in the SAROAD Users Manual APTO-0661.

(10) The information on the SAROAD data sheets should be keypunched onto data processing cards.

(11) From the keypunch data cards, prepare a magnetic tape record for submittal to EPA.

A check system can be built into the routine data processing which is useful for both data validation and detection of problems with the system (Reference 6). A graph can be prepared from previous data (e.g., one year of data) containing the average and ± 3σ values for the hourly averages for each hour of the day. An example of such a graph for CO is shown in Figure 16. The occurrence of any one or more of the conditions listed below should be investigated for possible causes (e.g., extra heavy traffic, shift in peak traffic hours, or periods of atmospheric stagnation with high pollution levels).

(1) An estimated one hour average falls outside the ± 3σ limits for that specific hour.

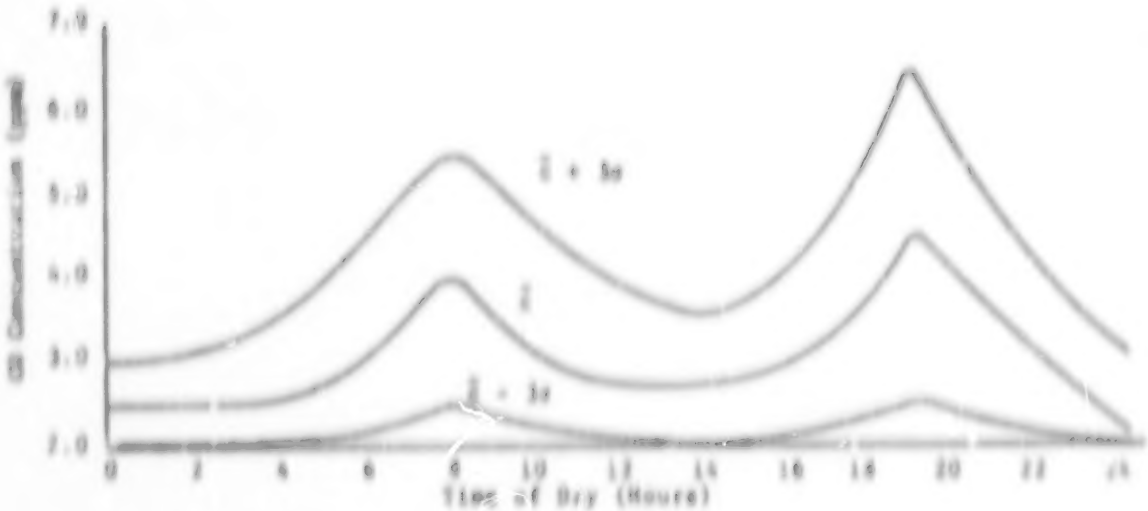

FIGURE 16
A SAMPLE GRAPH OF THE MEAN ($\bar{x}$) AND 3σ LIMITS OF
HOURLY CO CONCENTRATION FOR A 24 HOUR PERIOD
(Reference 9)

(2) The daily pattern has shifted to left or right by two or more hours.

(3) Abnormal patterns such as no peaks.

If no outside factors are found to explain the observed behavior, special tests should be run on that monitoring station to verify its proper performance.

5.1 Data Processing Quality Assurance Checks

One very useful quality assurance measure which requires minimal extra effort is to perform spot checks on the data processing. The check should be carefully performed by someone other than the person who originally reduced the data, and preferably by someone with considerable experience in data reduction.

The check is made by starting with the raw strip chart data and continuing through the entire transcription of the data to its final form. The "check" column of the data reduction sheet (see Figure 15) is for this purpose.

EPA recommends that the two highest hourly averages during each sampling period be selected for checking (Reference 5, Page 33 and Reference 6, Page 39). Depending on available manpower, either a greater or lesser amount may be selected. If a check value differs by as much as ±1.0 ppm from the original value, it is recommended that all hourly averages for that sampling period be checked and corrected, with the original check value(s) labeled.

An historical record of the results of checks should be maintained and regularly evaluated to monitor the error associated with the data reduction.

5.2 Management of a Quality Assurance Program

The previous sections have discussed the methods and procedures for obtaining the information on which a quality assurance program is based. This information can be used by the manager of the monitoring program to achieve the following types of goals.

(1) Assign Error Limits and Confidence Levels to the Air Quality Data - The information collected during the audit checks with control samples plus the information from the data processing checks provide the basis for assigning error limits and confidence levels to the data. The greater the number of these checks, the better the evaluation of the error limits and the higher the confidence level which can be assigned.

(2) Detect and Isolate Major Components of System Error - Routine calibrations, multi-point calibrations, control checks, special tests, data processing checks, and the operator's routine supervising of the system can all help detect and isolate components of error. An essential part of this is rapid communication of definite or suspected problems. A routine mechanism should be established whereby the operator's daily report on the system is reviewed and acted on as soon as possible.

Contributors to error in an ozone monitoring system include inaccuracies in the output of the ozone generator, inaccuracies in the NBSI calibration of that generator, zero drift in the analyzer, span drift in the analyzer, excessive noise in the analyzer, changes in the flow rate, excessive temperature changes, or excessive line voltage changes. All of these factors can be monitored through the quality assurance program discussed earlier, and steps taken to correct those which are found to be major components in system error.

Contributors to error in a carbon monoxide monitoring program include inaccuracy or change in the stated CO concentration of calibration gases, water vapor interference, data processing errors, drift in the analyzer output, noise, temperature-induced changes, voltage induced changes, and undetected analyzer or sample manifold problems. Span gas cylinders received from vendors should be verified versus an NBS standard before using for spans or calibrations. All of these factors can be monitored through the quality assurance program discussed earlier and steps taken to correct those which are found to be major components in system error.

(3) Assess Operator Performance and Define Additional Training Needs - If regular operators are used for specific stations in the monitoring system, the results of the control checks can be used to measure the proficiency of these operators. Other factors such as proper maintenance of

records, operating procedures, etc., can also contribute to this evaluation, which will point up requirements for additional training or establishment of more regimented operating procedures.

(4) Plan for Future Equipment Acquisition and System Expansion or Modification - Maintaining an effective quality assurance program requires the commitment of considerable funds for manpower and equipment. As the quality assurance program expands, the feedback from this program may indicate that any new resources which become available should be dedicated to improving the data quality from the existing monitoring stations rather than increasing the number of monitoring stations. If this decision is made, the results of the quality assurance program will point up those areas where the resources can be applied most effectively, e.g., temperature control of the stations, new analyzers, new ozone generators, voltage regulators, etc.

(5) Select Monitoring Strategies and Quality Control Strategies for Specific Monitoring Requirements - The monitoring network of a city, county, or state may include several goals. In many cases the purpose may be to compare air quality at a given site to state or federal air quality standards. If the standards are exceeded, this air quality data may form the basis of a control plan to limit the emission of certain species. Another purpose might be air monitoring as a part of health effects studies to determine the relationship between pollutant levels and health

problems. In this case the air quality data might be used to justify a new air quality standard. Still another purpose might be a baseline monitoring program to determine air quality in an area prior to its development.

In all cases, quality assurance in an air monitoring program is important, but it is especially critical for cases such as the first two above where the quality of the data might become the subject of litigation. The data must be not only accurate, but also defendable. This means that particular attention must be paid to maintaining detailed records, and these records must depict a properly operated monitoring system and a well planned quality assurance program.

Experience with a quality assurance program will indicate the extent to which a particular monitoring network meets these goals, and allow deficiencies to be identified and corrected.

6.0 REFERENCES

(1) Federal Register, Vol. 40, No. 33, February 18, 1975, p. 7052.

(2) Part 53 of Title 40, Code of Federal Regulations as originally proposed in the Federal Register, Vol. 38, October 12, 1973, p. 28438.

(3) Guidance for Air Quality Monitoring Network Design and Instrument Siting (Revised), EPA Document OAQPS No. 1-2-012, September, 1975.

(4) APTD-0736, October, 1972, Field Operations Guide for Automatic Air Monitoring Equipment, p. 32.

(5) Smith, Franklin and A. Carl Nelson, Jr., Guidelines for Development of a Quality Assurance Program, Reference Method for Measurement of Photochemical Oxidants, EPA-R4-73-028c, Contract No. 68-02-0598, Research Triangle Park, N.C., 1973.

(6) Smith, Franklin and A. Carl Nelson, Jr., Guidelines for Development of a Quality Assurance Program, Reference Method for the Continuous Measurement of Carbon Monoxide in the Atmosphere, EPA-R4-73-028a, Contract No. 68-02-0598, Research Triangle Park, N.C., 1973.

References 5 and 6 are available from EPA. These documents provide detailed outlines for quality assurance programs, special checks, and data evaluation. Copies may be obtained from either the Technical Publications Branch, Office of Administration, Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, or National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia, 22151.

APPENDIX I

RULES AND REGULATIONS

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6.3 *Activated Charcoal Trap.* Pre Sitterly activated charcoal.

6.4 *Distilled Water.* Used for all reagents to dissolve or dilute. Prepare by distilling water in an all-glass distillation apparatus and a reagent of potassium permanganate and a crystal of barium hydroxide, and redistill.

6.5 *Absorbing Reagent.* Dissolve 10.0 g potassium dihydrogen phosphate (KH_2PO_4), 11.5 g anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 28.6 g dodecahydrate salt ($Na_2HPO_4 \cdot 12H_2O$), and 1.00 g potassium iodide (KI) in purified water and dilute to 1,000 ml. The pH should be 6.8±0.5. The solution is stable for several weeks if stored in a glass-stoppered amber bottle in a cool, dark place.

6.6 *Standard Arsenious Oxide Solution (0.05 N).* Dry primary standard grade arsenious oxide (As_2O_3) 1 hr 1 hour at 105° C. immediately before using. Accurately weigh, to the nearest 0.1 mg, 9.9 g arsenious oxide from a small glass-stoppered weighing bottle. Transfer to 50 ml. 1 N sodium hydroxide in a flask or beaker on a steam bath. Add 25 ml. 1 N sulfuric acid, then, transfer quantitatively to a 1,000-ml volumetric flask, and dilute to volume. Note: Solution must be neutral to phenol red indicator.

$$\text{Normality sodium arsenite} = \frac{25 \text{ ml } As_2O_3 \times N}{49.95}$$

6.7 *Starch Indicator Solution (0.5 percent).* Triturate 0.5 g soluble starch and approximately 5 mg mercuric iodide (preservative) with a little water. Add the paste slowly to 100 ml of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

6.8 *Standard Iodine Solution (0.05 N).*

6.8.1 *Preparation.* Dissolve 3.5 g potassium iodide (KI) and 0.9 g resublimed iodine (I_2) in 10 ml purified water. When solution is complete, transfer the solution to a 250-ml. glass-stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and restandardize as necessary.

6.8.2 *Standardization.* Pipet accurately 20 ml. Standard arsenious oxide solution into a 250-ml. Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with bicarbonate of soda, and add about 3 g. excess. Titrate with the standard iodine solution using 2 ml. starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml. of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds.

$$\text{Normality } I_2 = \frac{\text{ml. } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml. } I_2}$$

6.9 *Diluted Standard Iodine.* Immediately before use, pipet 1 ml. standard iodine solution into a 100-ml. volumetric flask and dilute to volume with absorbing reagent.

7. *Procedure.*

7.1 *Instructions.* Instructions are to accompanied from the manufacturer given must be used to put the apparatus in operation. If commercial units are used, follow the special instructions given by the manufacturer, insofar as they are consistent with the specific instructions given in this method. Assemble the sampling train as directed in section 8. Introduce reagents into the system under the same conditions of pressure and flow rate as are used in calibration. By proper adjustments of rate and vacuum control, direct reading of ozone concentration is possible.

7.2 *Blank Determination.* Prepare a series of absorbance of various iodine solutions against unexposed ozone equivalents as follows:

7.2.1 Into a series of 50 ml. volumetric flasks, pipet 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 ml. of diluted standard iodine solution (6.9). Dilute each to 100 ml. with absorbing reagent. Mix thoroughly, and immediately read the absorbance of each at 352 nm against unexposed absorbing reagent as the reference.

7.2.2 Calculate the concentration of the solutions as total eq O_3 as follows:

$$\text{Total eq } O_3 = \frac{(V_1)(N)(24{,}000)}{V_2}$$

N = Normality I_2, used (0.01), meq/ml

V_1 = Volume of diluted standard I_2, added, ml (0.5, 1, 2, 3, 4, 5)

Plot absorbance versus total eq O_3.

7.3 *Instrument Calibration.*

7.3.1 *Generation of Test Atmosphere.* Assemble the apparatus as shown in Figure 2B. The ozone concentration produced by the generator can be varied by changing the position of the adjustable sleeve. For calibration of ambient air analyzers, the ozone source should be capable of producing ozone concentrations in the range 100 to 1,000 $\mu g/m^3$ (0.05 to 0.5 p.p.m.) at a flow rate of at least 5 liters per minute. At all times, the airflow through the generator must be greater than the total air required by the sampling systems.

7.3.2 *Sampling and Analysis of Test Atmosphere.* Assemble the 02 sampling train as shown in Figure 2A. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. The manifold distributing the test atmosphere must be sampled simultaneously by the 02 sampling train and the instrument to be calibrated. Check sampling systems for leaks. Record the instrument response to concentrations at each concentration (usually six). Establish these concentrations by analysis, using 15.2 neutral buffered potassium iodide method as follows:

7.3.2.1 *Blank.* With ozone lamp off, flush the system for several minutes to remove residual ozone. Pipet 10 ml absorbing reagent into each absorber. Draw air from the ozone-generating system through the sampling train at 2.0 to 5 liter/minute for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm. cell. Determine the absorbance at 352 nm, against unexposed absorbing reagent as the reference. If the system blank gives an absorbance, continue flushing the ozone generation system until no difference is obtained.

7.3.2.2 *Test Atmosphere.* With the ozone lamp operating, equilibrate the system for about 10 minutes. Pipet 10 ml. of absorbing reagent into each absorber and bubble gently for 10 minutes in the concentration range desired for calibration. Immediately transfer the solutions from the two absorbers to clean 1-cm. cells. Determine the absorbance of each at 352 nm, against unexposed absorbing reagent as the reference. Add the absorbances of the two solutions to obtain total absorbance. Read total eq O_3 from the calibration curve (see 9.3). Calculate total eq O_3 in the sample corrected to reference conditions of 25° C and 760 mm. Hg as follows:

$$V_0 = V \times \frac{P}{760} \times \frac{298}{t + 273} \times 10^{-3}$$

V_0 = Volume of air at reference conditions, m^3.

V = Volume of air at sampling conditions, liters.

P = Barometric pressure at sampling conditions, mm. Hg.

t = Temperature at sampling conditions, °C.

10^{-3} = Correction of liters to m^3.

Calculate ozone concentration in p.p.m. as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g \text{ } O_3}{V_0} \times 0.510 \times 10^{-3}$$

8.3.3 *Instrument Calibration Curve.* Instrument response from the photocurrent or voltage is ordinarily in current or voltage. Plot the current, or voltage if appropriate, (y-axis) for the test atmosphere against ozone concentration as determined by the neutral buffered potassium iodide method, in p.p.m. (x-axis).

8. *Calculations.*

8.1 If a recorder is used which has been properly zeroed and spanned, ozone concentrations can be read directly.

8.2 If the 102 amplifier is read directly, the reading must be converted to ozone concentrations using the instrument calibration curve (8.3.3).

8.3 Conversion between p.p.m. and eq/m^3 values can be made as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g \text{ } O_3}{m^3} \times 0.510 \times 10^{-3}$$

10. *Bibliography.*

Hodgeson, J. A., Martin, B. E., and Baumgardner, R. E., "Comparison of Chemiluminescent Methods for Measurement of Atmospheric Ozone", Preprint, Meeting Analytical Symposium, New York, N.Y., October, 1970.

Hodgeson, J. A., Moreno, R. E., and Martin, B. E., "A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors", Preprint No. 71-606, Instrument Society of America, Integrated and Instrumentation Division, Chicago, Ill., October, 1971.

Meixenberg, H. R., Van der Hoek, A., and Van Duijn, J., Nature 198, 67 (1963).

Warren, H. J., and Babcock, H., Ann. Ast. Phys. 62, 591 (1970).

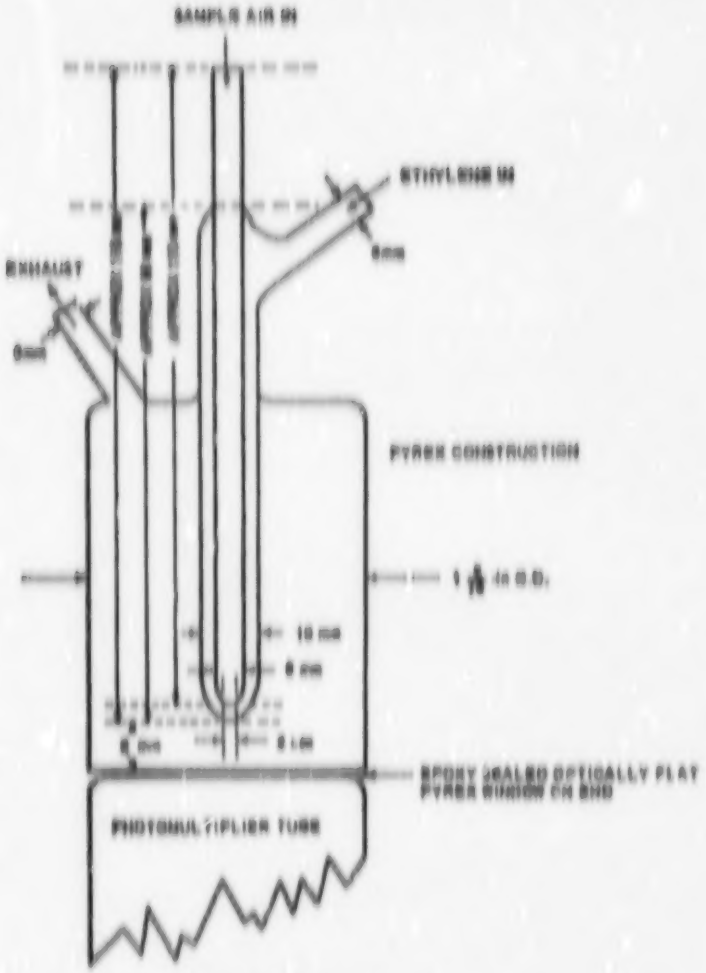

Figure 01. Detector cell.

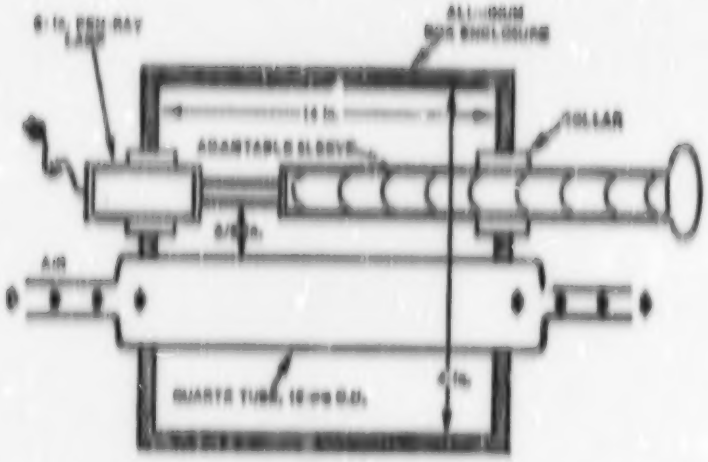

Figure 3B. [illegible]

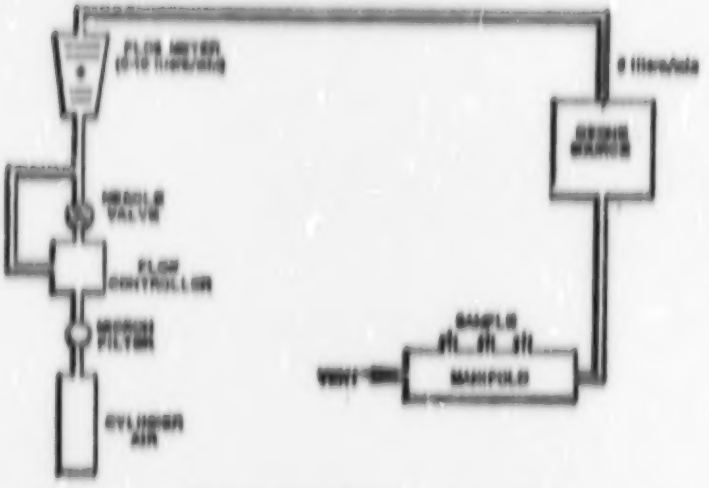

Figure 4B. [illegible]

APPENDIX II

EPA recommends (Reference 6, pp. 8-11) two methods for verification of span gas bottles, one for the case where all the span gases are from the same manufacturer and one for the case where bottles from at least two manufacturers are used. The EPA methods assume that several standard or audit gases are available, and are as follows:

Method 1

(a) Set up and check out the analyzer.

(b) Calibrate the analyzer with the auditing gases.

(c) Construct a calibration curve from at least four (4) points, i.e., zero, span, and two (2) upscale points.

(d) Check the calibration curve and if any of the measured points deviate from the smooth curve by more than ± (1.0 + 0.01 C_a) ppm, where C_a is the certified concentration of the auditing gas, have that cylinder of auditing gas re-analysed. In some cases a subjective decision will have to be made by the supervisor as to whether it is the span gas or one of the up-scale gases that is in error. If all measured points are within the above limits, use the best fit curve as the correct calibration curve.

(e) Measure the calibration gases.

(f) Have all calibration gases whose measured value differs from its certified value by more than (1.0 + 0.02 C_g) ppm, where C_g is the labeled concentration of the span gas, reanalyzed until an acceptable set of calibration gases is obtained.

(g) Obtain and verify new calibration gases before old ones are exhausted by calibrating the analyzer with the old calibration gas. Accept the new gas as good if the measured and certified values are within ± (1.0 + 0.02 C_g) ppm of each other; reject the gas otherwise.

Method II

(a) Set up and check out the analyzer.

(b) Have two (2) sets of calibration gases (±2%) from different suppliers available.

(c) Have one set of auditing gases (± 1%) from another supplier if possible; or when available, "standard gases" of EPA's recommendation.

(d) Calibrate the analyzer with the auditing or standard gases.

(e) Construct a calibration curve from at least four (4) points, i.e., zero, span, and two (2) upscale points.

(f) Check the calibration curve and if either one of the two upscale points deviates more than ± (1.0 + 0.01 C_g) ppm from the smooth calibration curve, have that cylinder of auditing gas reanalysed. In some cases a subjective decision will have to be made by the supervisor as to whether it is the span gas or one of the two upscale gases that is in error. If both upscale points are within the above limits, use the best fit curve as the correct calibration curve.

(g) Measure both sets of calibration gases.

(h) If both sets of calibration gases disAgree (i.e., measured and certified values differ by more than ± (1.0 + 0.02 C_g) ppm for cylinders of each set, have all calibration and auditing gases reanalysed.

(i) If one set of calibration gases agrees (i.e., measured and certified values agree within ± (1.0 + 0.02 C_g) ppm for each cylinder), accept that set as good and have the other set reanalysed. If both sets agree, accept both sets as good.

(j) Obtain and verify new calibration gases before the old gases are exhausted by calibrating the analyser with the old gases and measuring the new calibration gas. Accept the new gas as good if the measured and certified values are within ± (1.0 + 0.02 C_g) ppm of each other; reject the gas otherwise.